ST. CLAIR RIVER ORGANICS STUDY

IDENTIFICATION AND QUANTITATION OF ORGANIC COMPOUNDS

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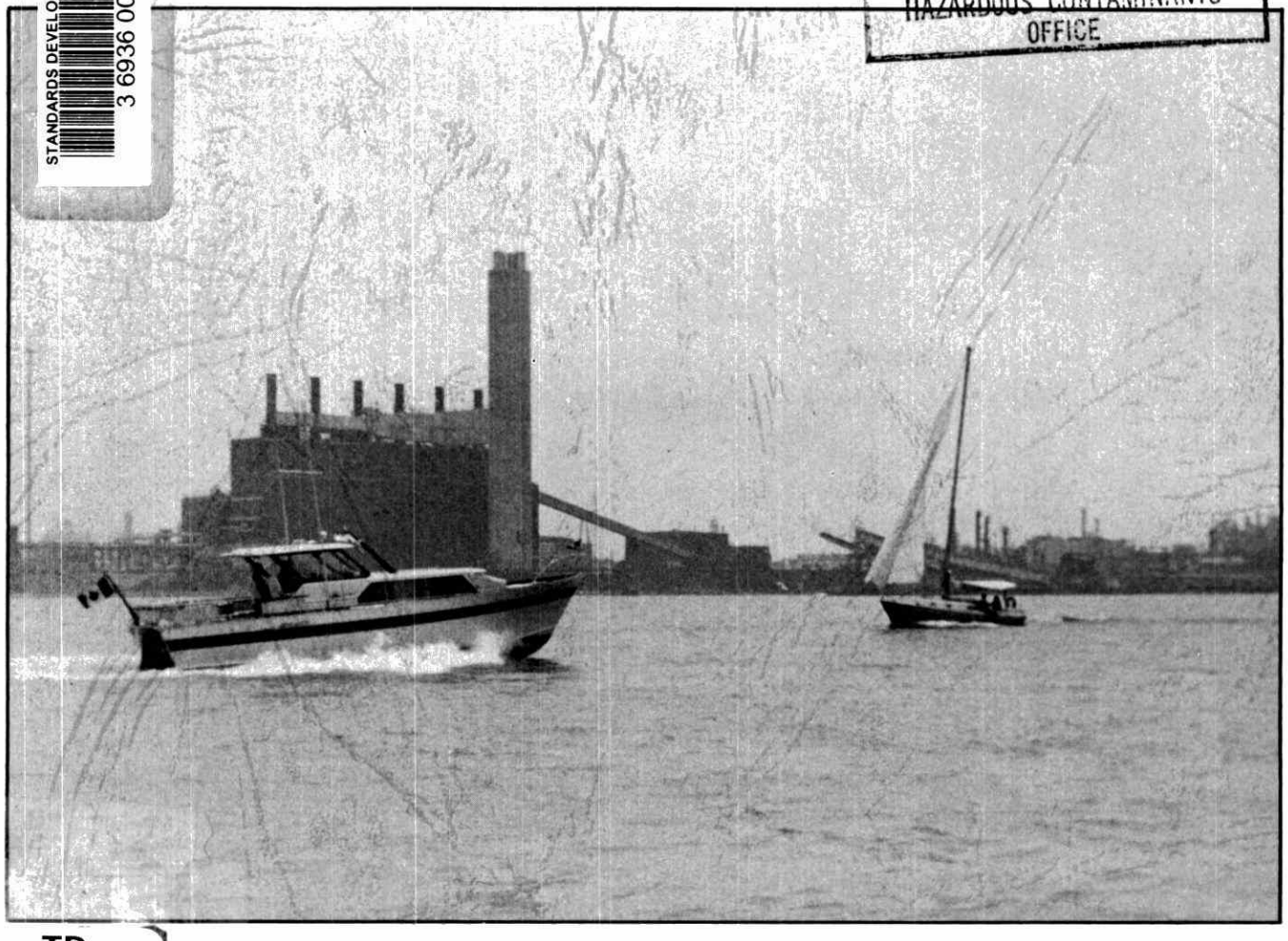

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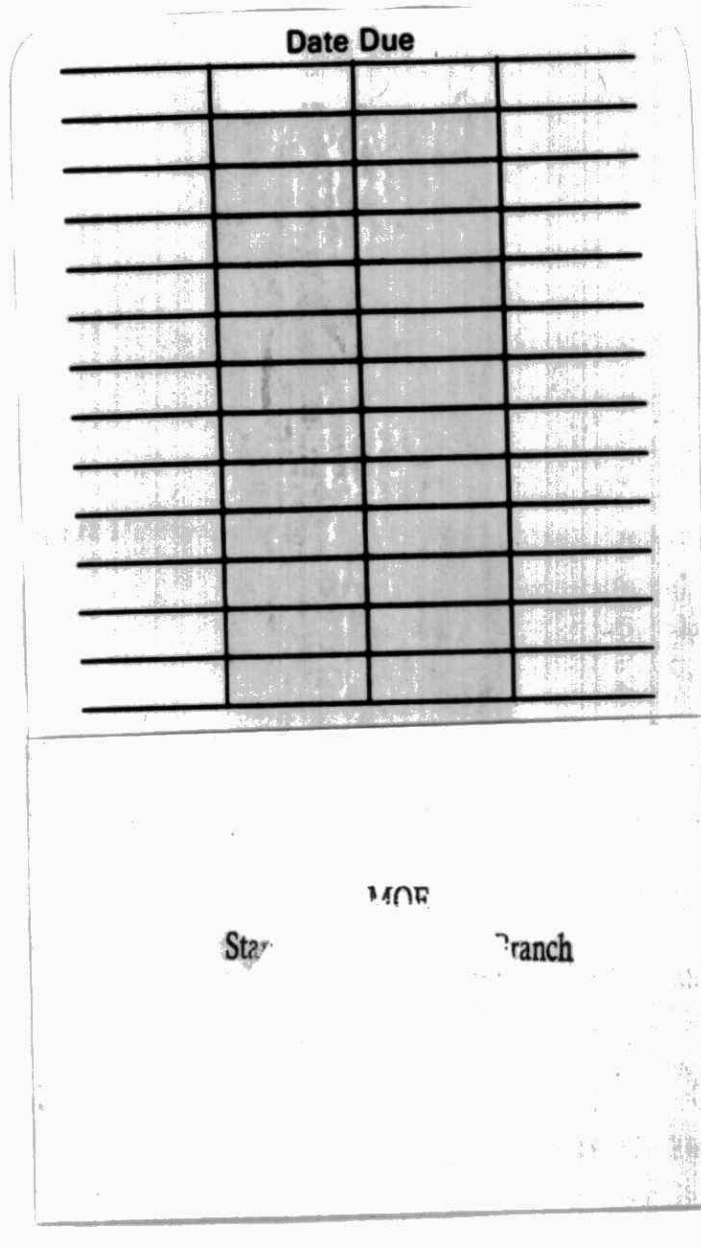

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EXPLANATORY NOTE

IDENTIFICATION AND QUANTITATION OF ORGANIC COMPOUNDS

Eighty-four volatile organic compounds were identified and measured from 1975 and 1977 samples taken from about 60 sites along the St. Clair River area.

Sampling sites included industrial discharges from 11 industries in the Sarnia Chemical Valley industrial complex, St. Clair River water and sediment, sewage treatment plant discharges, potable water supplies and fish.

Organic compounds are composed of carbon and hydrogen, and could include nitrogen, oxygen, sulphur and halogens like chlorine. Volatile organic compounds are organics with a low boiling point. These compounds include solvents and other compounds commonly used or produced in the petro/chemical industries like those found in the Sarnia Chemical Valley area.

The compounds were determined by the use of sophisticated gas chromatographic/mass spectrometric techniques. The most common compounds found include chloroform, methylene chloride, dichloroethane and benzene.

The gas chromatograph/mass spectrometer is actually two analytical tools brought together to function as one. A gas chromatograph is used to separate individual compounds based on the principle that different compounds have unique boiling points and travel through columns of special materials at different rates. The mass spectrometer is used in tandem with the gas chromatograph to identify organic compounds. In effect, it takes a spectroscopic fingerprint of a substance and compares it to similar fingerprints on file for positive identification.

While about 65 compounds were found in the direct discharges of industrial effluent from the 11 industries samples, only 15 compounds were found in the general flow of St. Clair River water. In the St. Clair River, most of the low levels of organic compounds in industrial effluent were diluted below the sensitive

detection levels of Ministry equipment. Seventeen organic compounds were found in treated drinking water, including downstream samples from Tilbury, Amherstburg and Windsor. Twelve compounds were observed in fish.

Common water treatment practices add some compounds like chlorine to the water and alter already existing compounds not removed by the treatment process.

One of the major conclusions of the study was that in spite of the large volumes of effluents and numbers of organic compounds entering the river daily, the quality of river water was remarkably good.

ORGANIC COMPOUNDS FOUND IN DRINKING WATERS

1.	Lambton Area Water Supply System (above industrial area)	Methylene Chloride Chloroform Dichlorobromomethane 1,2-dichloroethane Benzene Toluene Xylenes Dibromochloromethane Bromoform Trichloroethylene 1,1,1-Trichloroethane Tetrachloroethylene Ethylbenzene
2.	St. Clair River (water supplies downstream of industrial area - private supplies; Walpole Island WTP)	Methylene Chloride Chloroform Carbon tetrachloride 1,2-dichloroethane Tetrachloroethylene Dichloropropane Dichlorobenzenes Benzene Xylenes Toluene Diethylbenzene Trimethylbenzene
3.	A. J. Brian Pumping Station (Windsor)	Methylene chloride Chloroform Dichlorobromomethane 1,2-dichloroethane Benzene Toluene Xylenes

MOE Routine Monitoring Data	Chloroform
(Tilbury North Township,	Dichlorobromomethane
Windsor WTP, Amherstburg WTP)	Dibromochloromethane
	Carbon Tetrachloride
	Trichloroethylene

Total number of organic compounds identified during total study in drinking water supplies = 17

Total number of organic compounds identified in the St. Clair River downstream of industry = 12

ST. CLAIR RIVER ORGANICS STUDY

IDENTIFICATION AND QUANTITATION

OF ORGANIC COMPOUNDS

By

R. F. Bonner and O. Meresz

Organic Trace Contaminants Section

Laboratory Services Branch

Ministry of the Environment

February 1981

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FOREWORD

An in-depth investigation of organic chemicals in industrial effluents along the St. Clair River commenced in 1975. The adoption of gas chromatography/mass spectrometry analytical methodologies, by the Laboratory Services Branch of the Ministry of the Environment, made the detection of low concentrations of such compounds possible. In a preliminary report, "Organic Compounds of Industrial Origin in the St. Clair River", developed as an internal working document in January of 1977, positive identification was made of some 47 organic compounds discharged to the St. Clair River.

The St. Clair River Organics Study Group was formed early in 1977 to further investigate and confirm the presence and significance of the organic compounds identified, particularly in relation to possible effects on public water supplies downstream and the potential bio-accumulation of such compounds by fish resident in or frequenting this important waterway. Also, it was decided that a comprehensive assessment of water quality conditions and aquatic life was warranted to permit a comparison with unpublished biological data collected in 1968.

Representation on the Study Group included staff from various branches of the Ministry of the Environment and the Special Studies and Services Branch of the Ministry of Labour. Early in its deliberations, the Study Group identified the following goal:

> To assess the presence and significance of organic chemical compounds in the St. Clair River system and to establish from this program recommendations for control measures and further studies that may be required in relation to human health and environmental effects.

In order to accomplish the above goal, the following ten objectives were identified:

1. Identification and quantitation of organic compounds in industrial discharges, St. Clair River water, potable water supplies, bottom sediments and fish.

2. Completion of a literature search on the characterisitics and effects of the organic compounds identified. Lethal, sub-lethal and synergistic effects of these compounds on human and aquatic life to be considered.

3. Determination of the significance of chlorinating trace amounts of these organic materials in industrial cooling water discharges, sewage plant effluents and in potable water supplies.

4. Determination of the types and concentrations of compounds causing fish toxicity and fish tainting problems.

5. Estimation of the dissolved organics concentration at any point in the river based on effluent quality and flow measurements.

6. Completion of benthic macroinvertabrate, aquatic plant, sediment and water quality studies on the river in terms of biological and common chemical indicators. Results to be compared to survey work carried out in 1968-69. Assessments of mercury levels in sediments to be completed.

7. Determination of the potential carcinogenicity of organic compounds through quick-screening microbiological tests for mutagenesis.

8. Establishment of whether biodegradation or alteration of organic compounds occurs through bacterial action in sediments.

9. Development of recommendations clarifying levels to which contaminants must be reduced, as a basis for necessary treatment and effluent controls.

10. Clarification of the need for additional research to establish potential dangers to human health or the natural environment where this information is lacking.

Work on the component studies related to thesse objectives progressed throughout 1977 and 1978 and into 1979. As a result of these efforts, the following reports will be published during 1979-1980, to form an integrated series covering the objectives defined previously:

(1) Identification and Quantitation of Organic Compounds.

(2) Fish Toxicity and Tainting Evaluations for Selected Industrial Effluents.

(3) Waste Dispersion.

(4) Biological Surveys 1968 and 1977.

(5) The Detection of Mutagenic Activity; Screening of Twenty-three Compounds of Industrial Origin.

(6) Biodegradation of Organic Compounds.

Wherever possible, each of these reports will present conclusions and advance recommendations to achieve an improvement of water quality in the St. Clair River system or to clarify additional research requirements in regard to potential human health or environmental effects.

It is anticipated that subsequent reports dealing with fish toxicity and tainting and the potential carcinogenicity of industrial organic compounds in relation to the St. Clair River will be issued by the Ministry, since these particular components will be the subject of further study by the Limnology and Toxicity Section of the Water Resources Branch and the Microbiology Section of the Laboratory Services Branch, respectively.

SUMMARY AND CONCLUSIONS

This report presents and discusses data on the organic compounds present in a variety of samples collected from the vicinity of the St. Clair River in 1977 and 1978. It forms part of a major study on this river system which was initiated following exploratory work in 1975/76 the results of which are, to an extent, also reported here. As described in the foreword, a Study Group, formed early in 1977, identified the goal of the study to be:

"To assess the presence and significance of organic chemical compounds in the St. Clair system and to establish from this program recommendations for control measures and further studies that may be required in relation to human health and environmental effects."

This goal was to be achieved through ten objectives of which three are relevant here:

i) Identification and quantitation of organic compounds in industrial discharges, St. Clair River water, potable water supplies, bottom sediments and fish.

ii) Completion of a literature search on the characteristics and effects of the organic compounds identified. Lethal, sub-lethal and synergistic effects of these compounds on human and aquatic life to be considered.

iii) Determination of the significance of chlorinating trace amounts of these organic materials in industrial cooling water discharges, sewage plant effluents and in potable water supplies.

Clearly, the scope of these objectives is enormous: there are several million known organic compounds and any attempt to identify every compound in a complex mixture is extremely difficult and time consuming. Exact quantitation of organic compounds at trace levels is generally not possible unless pure reference compounds are available at the time of analysis. Nevertheless, even when pure

standards are not available, significant concentration ranges can be established for an identified contaminant.

It has been clear from the beginning of this study that with the available time and resources the objectives of the programme could not be fully achieved. On the other hand, the undertaking of this type of study was considered essential for the Ministry to fulfill its responsibilities to the public in the control of emitted contaminants, the establishment of environmental safeguards, the management of water and waste and the development and maintenance of measures intended to restore and enhance Ontario's natural environment.

Thus, even partial attainment of the goals of the present study was expected to furnish valuable information such as establishing background concentrations in the relatively new field of organic contaminants and to identifiy potential hazards and trouble spots to be further investigated in the future.

The study also served as a testing ground for the Laboratory's analytical capabilities and as a basis to identify needs in the future development of sampling, extraction and analytical techniques in organic trace analysis.

During the course of the exploratory (1975/76) and main (1977/78) studies a total of eighty-four different organic compounds were identified. Owing to the state-of-the-art in environmental toxicology, a complete assessment of the significance of these findings is at present not possible. However, these data will be extremely valuable when the long-term effects of very low levels of organic contaminants are established.

In 1975/76 samples were analyzed by a variety of techniques. All samples were extracted under acid, neutral and basic pH conditions and examined by GC using a flame ionization detector (FID). Those containing organics at significant levels were then analysed by Gas Chromatography/Mass Spectrometry (GC/MS), using a Purge and Trap technique, to identify the volatile organics present and by several GC only analyses to quantitate different compound classes, e.g. alcohols, aromatics, etc. For the extended study analyses were exclusively by GC/MS for the volatile organics. This approach suffers two main disadvantages: firstly, some important organics do not purge well because of polarity or molecular weight and,

secondly, samples cannot be cleaned up to remove interferences, e.g. petroleum hydrocarbons. There are however some important advantages that led to the selection of this method:

i) different sample matrices can be handled with minor modifications to the method.

ii) sensitivity, for example for 1 litre of water/effluent, is extremely good.

Standards were obtained for a range of chlorinated and aromatic compounds that had been observed in the exploratory study so that these could be quantitated. Identification, but not quantitation, was possible for other compounds even when standards were not available.

Because of the finite resources available for this study, all samples collected could not be analyzed. However, at least one sample was analyzed from each site and those with high levels or many compounds, whether in the exploratory or main study, were analyzed more than once. Even so, many samples were necessarily stored for prolonged periods. In addition variation in the amount of headspace, particularly in concentrated composite samples collected automatically, is considered to have a major effect on the organic concentrations. Consequently, it is felt that many of the results presented in this report are underestimates of the original in situ concentrations.

In general, the correlation between the different types of data is good. This is rather surprising since the organic analyses were for volatile organics only, while the PCB's are non-volatile and the method of measuring TOC generally involves pre-purging to remove CO_2 and volatiles. Only in the case of Ethyl Corporation's sewer did the total of volatile organic levels approach the TOC values: it is clear that analysis for volatiles reveals only part of the situation. This is extremely relevant to the comments below.

The St. Clair River system is chemically immensely complex and any future studies should take this into account. Much more attention should be paid to extractable compounds, particularly from sources that accumulate organics, namely, sediments and fish.

From the viewpoint of public health, drinking water samples are of greatest importance, with fish also being of interest. Some seventeen organic compounds were observed in drinking waters, including those downstream of the St. Clair River (i.e. Tilbury, Windsor, Amherstburg), and toxicological data, where available, is presented in Appendix 2. It is clear that toxicity studies are generally concerned with short-term effects and involve high concentrations or doses (ppm or mg/kg). This arises from the necessity of producing observable effects in small numbers of test animals. The drinking water concentrations noted in this report are invariably orders of magnitude lower and provide no discernible cause for concern. For some compounds the body possesses a detoxification mechanism that successfully handles low concentrations but which may be overwhelmed by high concentrations. Also detoxification itself may produce toxic metabolites. For these reasons extrapolations from the high concentrations used in toxicity studies to the low concentrations actually observed here, while at present unavoidable, is less than ideal. Further study of this important area is required.

Of the seventeen compounds detected in water supplies during this study, chloroform, bromodichloromethane and chlorodibromomethane are routinely observed in chlorinated drinking waters at low concentrations throughout Ontario (see "Organics in Ontario Drinking Waters, Part II, A Survey of Selected Water Treatment Plants", Ontario Ministry of the Environment, April 1977) and appear to originate from disinfection with chlorine as noted in Appendix 3. Bromoform is, presumably, also present but at a lower concentration. In addition, methylene chloride, carbon tetrachloride, trichloroethylene, benzene, toluene and xylene are observed frequently throughout the Province, but less consistently.

Based on the findings and recognized limitations of this study, the following conclusions are advanced:

1) In spite of the large volumes of effluents and numbers of organic compounds entering the river daily, the water quality is remarkably good. Evidence for this conclusion is to be found in the "Water Quality Sample" results presented in Tables 41 to 57 (pages 77 to 94).

2) Based on present knowledge, the majority of sewers discharging to the St. Clair River appear to present a minimal risk, especially in view of the high rate of dilution.

3) Chlorination of organic compounds does occur, as previously documented, although the compounds identified both in this study and by the routine monitoring work are all volatile - chloroform, dichlorobromomethane, dibromochloromethane and bromoform. Carbon tetrachloride does not appear to be produced by this mechanism. The questions of whether there are non-volatile compounds produced and what the precursors are (see Appendix 3), remain to be answered.

4) With regard to the observation of PCB's in sediments, it was concluded that these compounds may have arisen from use of PCB-based hydraulic fluids in the past since none of the industries studied are connected with the manufacture or distribution of these compounds.

5) Studies of this type need to involve samples that can be collected and stored without significant changes in the concentration of organic compounds. For volatile organics, techniques to minimize headspace and exposure to air, as well as the use of preservatives, should be investigated.

RECOMMENDATIONS

The following recommendations are proposed in order to obtain additional information on the organic compounds present and to further improve the quality of the St. Clair River:

1) Strategies should be developed for ongoing investigations of the long-term human health implications of exposure to low-level concentrations of organic compounds in drinking water supplies, as identified by this report, and to the organic contaminants demonstrated to be present in fish through uptake and bioaccumulation.

2) Additional studies and related development work should be initiated to identify and quantitate as much as possible the less volatile organic compounds that were not distinguished by the analytical methods used in this study.

3) For those organic compounds with demonstrated mutagenicity or carcinogenicity, efforts by the industries discharging such compounds will be required to assess the economic and technical feasibility of isolating and removing these compounds from their waste discharges or reducing levels to the lowest practicable limits. In addition, in the Discussion section several criteria were developed in order to identify potentially hazardous sites for further examination. Of the sites so identified eight appear to be more important:

i) Esso Chemical Canada Limited Pressure Sewer contained high levels of aromatic compounds.

ii) Polysar Limited Stereo API contained high levels of aromatics, particularly benzene. Sufficient data may be available for this site but confirmation is desirable.

iii) Dow Chemical Canada Limited 54" Sluice showed high levels of chlorinated compounds on one occasion. This should be confirmed by further testing.

iv) Dow Chemical Canada Limited Third Street Sewer contained high levels of aromatics and, occasionally, carbon tetrachloride. Other Dow Sewers showed significant levels of carbon tetrachloride and should be investigated further.

v) Ethyl Corporation of Canada Limited Total Discharge was frequently high in chlorinated compounds, particularly dichloroethane.

vi) Point Edward STP - a single sample contained ppm levels of benzene, toluene and xylene. The frequency of this type of occurrence should be ascertained.

vii) Walpole Island WTP samples contained up to 60 ppb of organics other than trihalomethanes. This should be re-sampled to confirm the concentrations that are representative at this site.

viii) Imperial Oil Limited Intake water should be examined to ascertain the fairly high occurrence (1-142 ppb) of methylene chloride in the #9 Separator effluent.

The following sites require attention but are less significant:

ix) Imperial Oil Limited Bio-oxidation Unit - a single sample showed benzene at 86 ppb, this needs confirmation.

x) The Township Ditch should be examined above Polysar to identify the source of vinyl chloride and other chlorinated compounds.

xi) Polysar Limited 54" Sewer and 66" Sewer should be examined for extractable organics as the TOC and loading values are high but the concentration of organic compounds identified was relatively low.

xii) Polysar Limited 72" Sewer contained high levels of alcohols in 1975; this may require further study.

xiii) Dow Chemical Canada Limited 42" and 48" Sewers both showed fairly high TOC values but low volatile organics. The extractable organics should be investigated.

xiv) A single sample from Dow Chemical Canada Limited Second Street Sewer contained 168 ppb dichloroethane; this should be examined further.

xv) DuPont of Canada Incorporated Intake Water should be examined to confirm that the organics largely originate upstream.

xvi) The fish data may prove more informative if additional analyses are performed, particularly on "background" samples from waters upstream of the industrial area.

INTRODUCTION

The identification and quantitation of organic compounds is an increasingly important aspect of environmental analytical work and, in recent years, less emphasis has been placed on routine (gross) water quality parameters such as total organic carbon (TOC), chemical oxygen demand (COD), pH, solvent extractables and phenolics. The problem with detailed organic analyses arises because of the large number of possible compounds which leads, inevitably, to samples that contain mixtures of many organics, usually at very low concentrations. Classical "wet" chemical techniques are unable to cope with this situation.

The difficulty has been alleviated considerably by improvements in separation techniques, particularly Gas Chromatography (GC) and Liquid Chromatography (LC). While these techniques are excellent for separating mixtures of organics, absolute identification is not possible, and likely tentative identification is time-consuming since it must be based on the coincidence of known peaks with unknowns, frequently when analyzed on several columns. Techniques that can yield positive identification, such as Infrared Spectroscopy (IR) and Nuclear Magnetic Resonance (NMR), lack sensitivity and the speed necessary to obtain data from fast-eluting GC peaks. The successful interfacing of GC with Mass Spectrometry (MS) has provided environmental chemists with an extremely powerful tool. The Mass Spectrometer yields highly specific information about the identity of compounds and can do so with small amounts of material, frequently 1 ng or less, in a short time, typically 1-5 sec/scan. The availability of commercial GC/MS systems, often linked to powerful computerized systems for the acquisition, storage and manipulation of data, has proved to be a major development in environmental analysis. A computerized GC/MS system was acquired by the Laboratory Services Branch of this Ministry in late 1974 and has since been applied to the determination of organic compounds in samples of environmental interest. The identification of the sources of organic compounds is fundamental and, with this in mind, a study of the St. Clair River was conducted during 1975 and 1976. The purpose of this preliminary study was two-fold:

i) To evaluate the performance and applicability of the new (GC/MS) analytical system in determining the individual organic components present in water samples.

ii) To obtain data concerning the occurrence and sources of organic compounds in Ontario waters.

The St. Clair River system was selected for this study since it is heavily industrialized and, in addition, a source of drinking water for several communities including Sarnia, Detroit and Windsor (the latter two via Lake St. Clair and the Detroit River).

During the 1975-76 exploratory study grab samples were taken from a variety of sources. The majority were industrial effluents although some water and sediment samples were also collected. GC/MS work was concentrated on analyses for volatile organics. However, this was supplemented by GC-only screening and analysis for vinyl chloride and aromatics, and also by measuring "solvent extractables". The report, isssued in 1977 as an internal working document, indicated that 47 different organics had been detected, occasionally at significant levels.

Following this exploratory study, the St. Clair River Project Steering Committee and the St. Clair River Organics Study Group were formed within the Ministry, and a more extensive study initiated. The expanded study was to involve organic and inorganic analyses of river and related samples, in addition to industrial effluents, and biological, toxicological and dispersion studies. The goal and objectives of the overall study have been described in the foreword: the objectives relevant to the organic analyses with which this Report is concerned are:

i) Identification and quantitation of compounds in industrial discharges, St. Clair River water, potable water supplies, bottom sediments and fish.

ii) Determination of the significance of chlorinating trace amounts of these organic materials in industrial cooling water discharges, sewage plant effluents and in potable water supplies.

iii) Determination of the types and concentrations of compounds causing fish toxicity and fish tainting problems.

This second study, commenced in 1977, expanded the types and numbers of samples taken and tended to place more emphasis on river water quality. As with the 1975-76 study, analytical work was restricted to the volatile organics. An important difference was that the earlier study employed grab sampling where the 1977 study employed mainly composite sampling of the effluents. Several problems were encountered with the analyses of the bottom sediments, arising mainly from large amounts of hydrocarbons attributed to petroleum products. Analytical development work on these samples is continuing and it is anticipated that data will be issued at a later date as an addendum to this report. With regard to objective iii) above determination of compounds causing fish toxicity and tainting, a variety of samples have been analyzed. Data from these analyses is not, however, presented here but forms a part of the separate report on fish tainting.

SCOPE OF REPORT

The primary purpose of this report is to communicate the results of the analyses for volatile organics in the St. Clair River System. It is, therefore, complementary to several of the other reports in the overall study which deal with the effects of pollution, particularly the biological and fish tainting studies. Two reports, those on Mutagenicity Testing and Dispersion, are critical to the interpretation of data included herein. For the sake of completeness, data from the 1975-76 study and results from analyses of the bottom sediments for polychlorobiphenyls (PCB's) are included. In addition to samples taken specifically for the St. Clair River Studies (1975-76 and 1977), certain sites, particularly Water Treatment Plants, are the subject of on-going routine monitoring. Data from these surveys (generally presented in various "Organics in Ontario Drinking Waters" reports) are included where appropriate.

The report proper begins with a section providing background information to the St. Clair River system ("St. Clair River System: Background and Sampling Sites"). This includes data on the river itself, on the Industries (location, product types, water usage, etc.) and on the Sewage Treatment Plants (STP's). Also summarized here are TOC values and flows measured at the time of the 1977 sampling, and the results of calculations indicating the daily discharge of organic carbon to the river: the bulk of this data is contained in Appendix 1. The sites are considered by category (i.e. contributors to the organic loading, indicators of the water quality, etc.) heading in the direction of flow.

The following sections describe the sampling program for the 1977 study and the analytical procedures employed.

The analytical results are again presented by category, as defined earlier, in the direction of river flow. Results for samples taken from sites not on the St. Clair River are also included.

The Discussion section summarizes each site, highlights the significant organic compounds observed (including PCB concentrations) and discusses the results in terms of hazard to the environment and human health.

Finally, the Report is summarized in a Conclusion Section and various Recommendations made.

Certain miscellaneous data are contained in the Appendices: Appendix 1 contains TOC, flow and organic loading data for the industrial effluents. Appendix 2 presents toxicological data on some of the major components. Appendix 3 describes some of the additional studies undertaken to address objective 3, the effects of chlorination on trace organics.

THE ST. CLAIR RIVER SYSTEM: BACKGROUND AND SAMPLING SITES

Figure 1 depicts the location of the St. Clair River. The river, which forms part of the U.S. - Canadian border, flows roughly North-South between Lake Huron and Lake St. Clair and is approximately 64 km in length. Lake St. Clair drains into Lake Erie via the Detroit River, and consequently the St. Clair River forms part of the connection between the Upper and Lower Great Lakes. A more detailed map of the St. Clair River and its immediate surroundings is given in Figure 2.

The daily flow of the river varies between 390 million cubic meters in dry seasons and 490 million cubic meters in wet seasons. Generally, the bottom profile is consistent with a deep central channel bordered by gradual shelving shallows close to the banks. As a result, the majority of the flow (95%) occurs in the main channel, and the remaining 5%, approximately, is available for mixing and dilution near the shorelines. It is, therefore, highly likely that industrial and other effluents will remain close to the banks and may "carry over" from one outfall to intakes further downstream.

Land adjacent to the northern part of the river, in the vicinity of Sarnia, is heavily industrialized, and the river is used both to provide service and cooling water and to receive industrial wastes. Daily discharge rates from the various industrial operations on the Canadian bank of the St. Clair have been estimated as totalling 4 million cubic meters, i.e. corresponding to roughly 1% of the total river flow or 20% of the flow estimated to be available for nearshore mixing.

The river is a source of potable water for the communities along its length. In 1975, the Ministry of the Environment completed the Lambton Area Water Supply System thereby replacing some of the previously used smaller supplies. The new system distributes daily averages of 180,000 cubic meters to Sarnia, municipalities downstream and inland communities where source water is in short supply. Other water supplies operative in 1977 were: Stag Island Water Supply System (operative May to October); Canadian Industries Ltd., Sombra Township; Chinook Chemicals Ltd., Sombra Township; Woodtick (Fawn) Island Water Works and Walpole Island Indian Reserve Water Works. Walpole Island is located in Lake St. Clair. A few

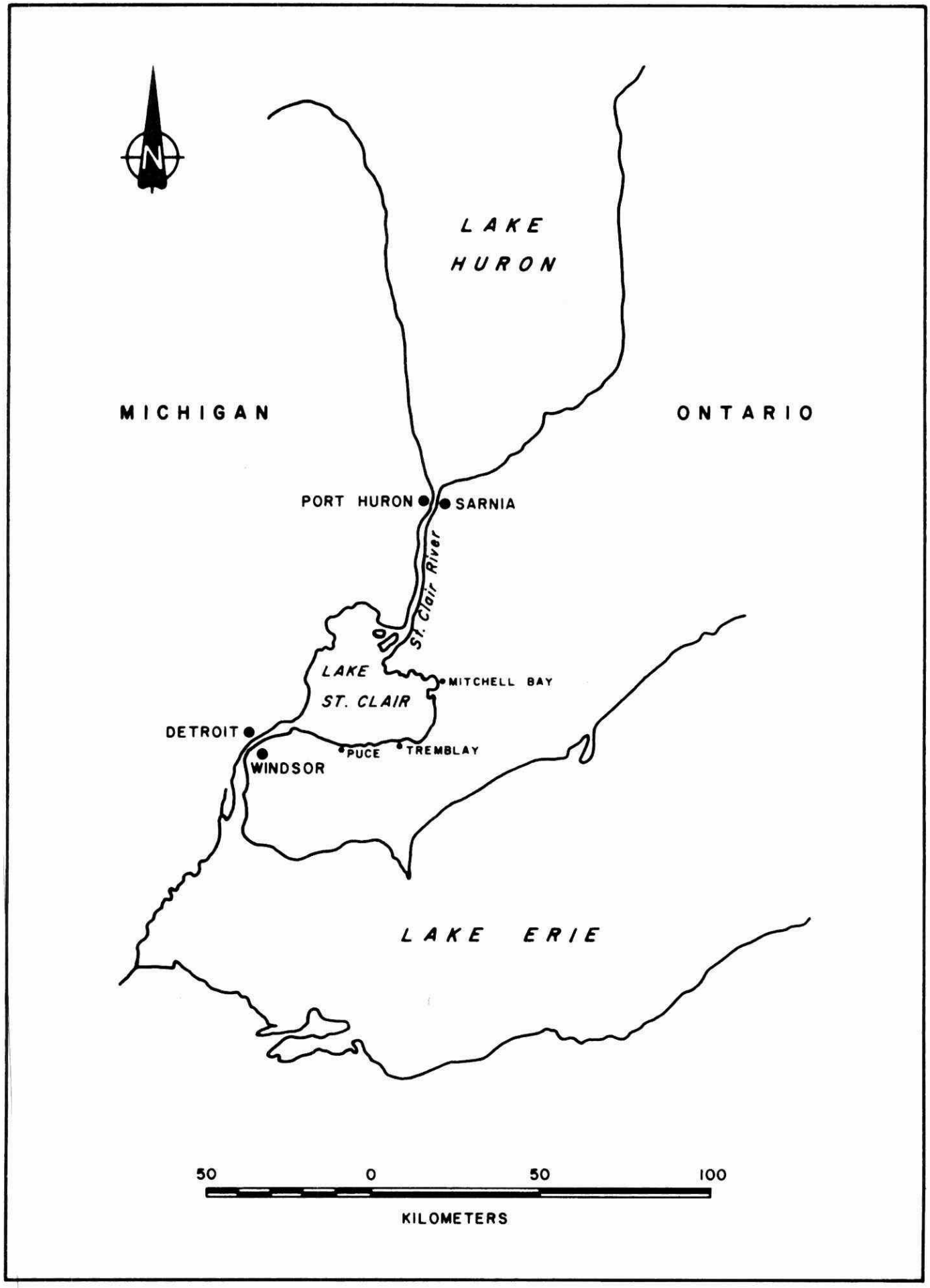


FIGURE 1 – LOCATION MAP OF THE ST. CLAIR RIVER

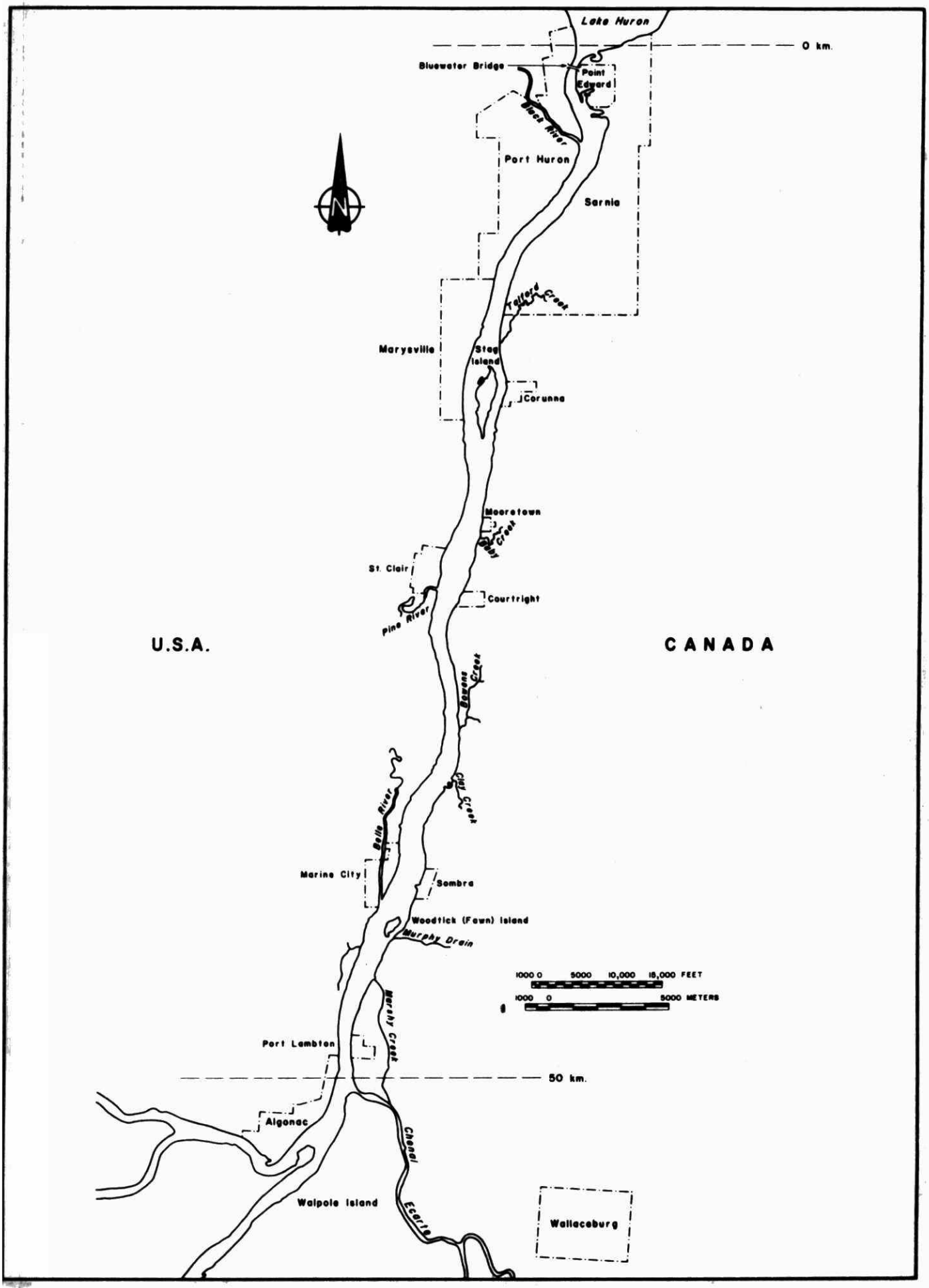


FIGURE 2 - EXPANDED MAP OF THE ST. CLAIR RIVER

riverside private residences also obtained water directly from the river or via wells. The water from the St. Clair ultimately flows into the Detroit River and is used as a raw water supply for Detroit and Windsor.

In addition to industrial effluents, the river also receives wastes from the various municipal STP's along its length. At the time of the study, six such plants were operative (Point Edward, Sarnia, Corunna, Courtright, Sombra and Port Lambton). Sampling, however, was restricted to the three largest plants (Point Edward, Sarnia and Corunna).

The river has extensive commercial marine traffic due to its location in the link between the Great Lakes. Other major river usage is mainly recreational, and largely restricted to the summer months.

For the purposes of providing background information and later presenting analytical data, the sample types are divided into five groups:

i) Industrial Effuents

ii) Sewage Treatment Plant Effluents

iii) Samples Indicating River Water Quality

iv) Samples Dependent on Water Quality

v) Other Samples

The background information on industrial effluents presented here is, necessarily, more detailed, owing to the importance of these discharges with regard to environmental and public health. The data included indicate the type and size of each industrial operation and the number of sewers discharging to the river. Flow rates and Total Organic Carbon (TOC) values for each sewer (provided by Mr. T. E. Wood, Sarnia District Office) obtained at the time of the 1977 sampling are listed in Appendix 1. In order to indicate the possible daily organic contribution of each sewer to the river, the results of calculations based on flow and TOC are also presented. The calculations were performed for each outfall as

follows: i) minimum daily flow was combined with the minimum TOC value obtained to yield a "minimum organic loading" figure; ii) maximum TOC and flow values were similarly combined to obtain a "maximum organic loading"; iii) the mean TOC (generally of 6 values) and average flows were combined for the "mean organic loading". Thus these figures indicate possible ranges for the organic loadings and a mean value. Where TOC values for the intake water were measured net organic loading values are provided: these are calculated using the discharge, not intake, flow since the latter is generally estimated to be within 10% of the former. It must be stressed that while these figures are primarily intended to facilitate comparison between the various sewers and industries, they also serve to highlight sewers that are of concern because of the magnitude of the discharge. In some cases the 1968 Biological Survey (see Biological Report) indicated areas of environmental concern and appropriate steps were taken before the 1977 extended study. Details of the treatment methods are included where this is relevant.

The information on STP's is limited to the size, type of treatment and certain parameters indicating the quality of the discharge.

Group iii) (Water Quality Indicators) are samples that may be used to indicate the River water quality. Included in this group are samples taken specifically for this purpose, i.e. river water, and also samples from other points where water is removed from the river, i.e. industrial, municipal and private intakes.

Group iv) (Samples Dependent on Water Quality) would include all biological and sediment samples, i.e. those where accumulation of organic compounds is possible. In the 1977 extended study, samples of this type included fish and bottom sediments.

Other samples, Group v), are samples not taken from the St. Clair River system but rather from areas likely to be affected by the quality of the St. Clair River. The group includes Water Treatment Plant (WTP) and fish from points downstream of the St. Clair, i.e. in the vicinity of Lake St. Clair and the Detroit River.

I. Industrial Effluents

At the time of the 1977 study, seventeen major industries were operative on the Canadian bank of the St. Clair River. Sampling was restricted to eleven of

these since the others either had minimal discharge to the river, discharged via municipal systems or via common sewers with other companies. In the 1975-76 study samples from Fiberglas, discharging to the Township Ditch above Polysar, were also analyzed. The following review presents basic information on each major industry and is arranged in order from North to South.

1) Imperial Oil Limited

Imperial Oil Limited (IOL) maintains a large refinery operation in the Sarnia area, processing some 140,000 barrels/day of crude. The refinery produces a complete range of petroleum products including gasoline, jet fuels, heating oils, lubricating oils, greases and waxes and involves the usual processes of reforming, cracking, distillation, etc. The company maintains three fully operational sewers; these are listed in Table A1, together with the flow rates and TOC values measured at the times of the 1977 sampling. A fourth sewer, #5 Separator, is an emergency bypass and usually has no flow. The Bio-oxidation (BIOX) and #11 and 12 separator effluents are combined and discharged to the river via an extended outfall. Values on the organic loadings, calculated as described previously (page 8) are presented in Table A2.

The Imperial Oil Ltd. discharges may be divided into two groups: clean water discharges and treatment system discharges, originating from complex treatment systems designed to remove phenolics, total organic carbon (TOC), solids and ammonia. During the 1968 survey, several major problems were noted and dealt with in three separate phases.

Phase 1, conducted in 1972, concentrated on segregating the two types of discharge (clean and treatment system),and involved cataloguing the flows and their origins.

Phase 2, conducted in 1973, was designed to improve oil removal from the contaminated discharge, and consisted of the addition of a dual media filtration system following the gravity separators. This system, once fully operational, produced a marked reduction of oil discharged to the river.

Phase 3, completed in 1975, addressed the problem of dissolved organics. An activated sludge system was installed to complement an earlier phenolics removal system, which had greatly reduced the phenolic concentration of the discharges and was designed to meet Ministry objectives for phenols.

2) Esso Chemical Canada Limited

The Esso Chemical operation in the St. Clair River is concerned with the production of petrochemicals from petroleum and petroleum products. Typical operations include alkylations for high octane gasoline additives and polyvinyl chloride (PVC) manufacture. The plant has one major discharge, a pressure sewer, and relevant data is provided in Table A3. TOC values for the intake water were not measured.

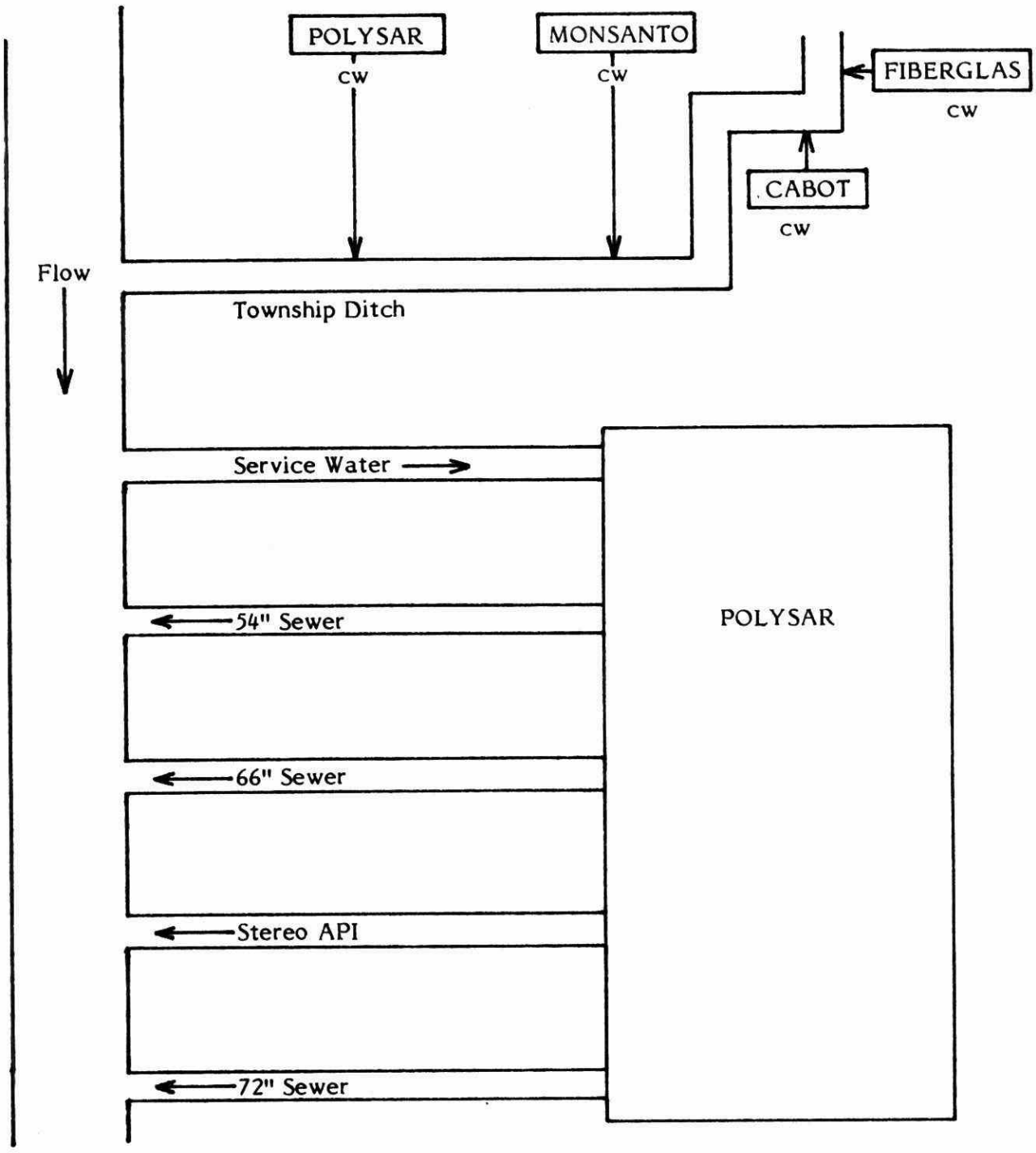
Major problems identified during the 1968 survey were losses of oils, ammonia and copper. The plant was, at that time, relying on an impounding basin and oil separation facilities. Following the study, complex emulsion-breaking dual media filters for oil removal were installed, the problems leading to high ammonia losses corrected and the copper discharge situation resolved. The initiation of bioassay studies of the effluent led to the discovery that highly toxic materials, lethal to fish, were present. The principal constituent was identified as naphthalene and programs to remove this compound were initiated and later completed. A resulting effluent quality improvement, as measured by bioassay, was observed.

3) Polysar Limited

Polysar Limited consists of several units manufacturing polymers or intermediates for sale or further processing. Typical operations include benzene, ethylbenzene, styrene, polybutadiene, polyisoprene, butyl latex and styrene-butadiene/neoprene-butadiene rubber (SBR/NBR) copolymer production. The complex also includes a steam plant to provide steam and electrical power for the manufacturing plants. The company maintains five sewers, as shown schematically in Figure 3. The Township Ditch receives cooling water from Polysar, drainage from the Esso Tank Farm and the Scott Road Landfill sites and cooling water discharges from Fiberglas (producing fiberglass products), Cabot Carbon (producing carbon black) and Monsanto. Discharge and organic loading data for the Polysar sewers are provided in Tables A4 and A5.

Major problems identified in the various discharges by the 1968 Biological Survey were suspended solids, dissolved organics, ether solubles and pH. Problems were approached by process changes (for example, the Wemco, the Graver and the main oil separator) but the necessity for further abatement was indicated by on-going Ministry studies. A 1976 control order, based on these studies, called for

Figure 3. Schematic Map of Polysar Sewers



Not drawn to scale

cw indicates Cooling Water Discharge

further improvements in the control of dissolved organics, phenols, suspended solids and oils.

4) Dow Chemical of Canada Limited

The Dow Chemical complex comprises a series of separate plants arranged to operate in conjunction with one another and yield a wide range of organic products. The major raw materials are brine and light hydrocarbons from neighbouring refineries. The main products of the complex are chlorinated solvents, vinyl chloride, styrene, glycols and glycol derivatives, polymers, chlorine and caustic soda. The company has nine sewers dicharging to the St. Clair River; discharge and organic loading data is presented in Tables A6 and A7. There are two service water intakes: the North (bottom of Third Street) and South (bottom of Fourth Street). Only the North intake was sampled in 1977. The first four sewers are located under First Street and serve the vinyl chloride, glycol I, solvents, amines, chlorine II and polystyrene plants. The Second Street Sewer received discharges from the "styron" and glycol II plants. In the "styron" plant various polymers are produced from styrene and butadiene: the glycol II plant produces polyglycols. The Third Street Sewer receives discharges from the styrene, latex, ethylene and polyethylene plants. The Fourth Street Sewer originates in the chloralkali I and Bio-oxidation plants.

The 1968 survey noted problems with BOD, COD, suspended solids, dissolved solids, chlorides and phenolic material. The pH levels occasionally exceeded the guideline (5.5 to 10.6) used at that time by the Ontario Water Resources Commission (OWRC). The use of mercury in the chloralkali plant was also of concern. Several pollution abatement measures have since been introduced: the use of mercury has been discontinued; discharges of degradable organics have been reduced by process changes and the installation of a bio-oxidation plant; discharges of soluble organics and oils have been decreased by process changes and treatment. The plant is also equipped to degrade chlorinated materials to harmless products by incineration.

5) Sunoco Incorporated

This plant is concerned with refinery operations, typically cracking, reforming and distilling and processes some 90,000 barrels of crude oil per day. One sewer discharges to the river; appropriate data being given in Table A8.

Major problems noted in 1968 were high levels of ether-soluble materials and phenolics. These were corrected by expansion of the biological treatment facility, improved capacity for oil removal and increased retention pond capacity. At the time of writing, Sunoco's discharge meets Ministry guidelines for most parameters, except during periods of surface runoff from process areas and the tank farm.

6) Shell Canada Limited

The Shell plant is, again, involved in typical oil refinery processes. Capacity is some 80,000 barrels/day. The plant draws intake water from the St. Clair River and discharges through two sewers to Talford Creek. Used cooling water is termed "clean" water, while process wastes are referred to as "contaminated" water. Relevant data is given in Table A9.

Capacity at the time of the 1968 survey was 42,000 barrels/day, later expanded, and the major concerns were oils, solids and phenols. To treat these problems and to process wastes being transferred to a deep disposal well, Shell added a biological treatment facility with associated ammonia and hydrogen sulphide stripping equipment. These improvements were brought on line early in the 1970's. Currently, Shell discharges meet Ministry guidelines for most parameters.

7) Ethyl Corporation of Canada Limited

The Ethyl corporation plant produces alkyl lead compounds, ethylene dichloride (1,2-dichloroethane) and pharmaceuticals. The latter is of little concern here since the organic contribution to the waste water is extremely small. Ethylene dichloride (1,2-dichloroethane) and the corresponding dibromo compound are used as lead scavengers in leaded gasolines. It is suspected that ethylene dibromide (1,2-dibromoethane), although not manufactured on site, is used in blends since it was detected in all samples except one. The effluents are discharged via a single sewer: data is presented in Table A10. Service water is obtained from Shell Canada Limited.

Major concerns in 1968 were dissolved solids and lead. Lead removal facilities have since been upgraded although sporadic problems occasionally result in lead discharges in excess of Ministry guidelines.

8) DuPont Canada Incorporated

The DuPont plant produces polyethylene from locally obtained ethylene. A single sewer discharges cooling water and process wastes, if any, to the river. Data is presented in Table A11. TOC values were not obtained for the service water, and furthermore, intake samples were not provided for analysis. In view of the proximity to the Ethyl Corporation operation, it is highly possible that the organics detected originated upstream.

The nature of the plant's operation and product results in essentially clean discharge water with occasional polymer pellets present.

9) Petrosar Limited

The Petrosar refinery has been added to the St. Clair industrial complex since the earlier (1968) study was completed. Major products are petroleum cuts, refined aromatics and olefins, including ethylene for use at the DuPont, Polysar and Union Carbide plants. Relevant data is presented in Table A12 for the single sewer.

The plant utilizes modern technology and has an extremely low water usage. Phenol removal is effected by both biological treatment and carbon filtration. The outfall to the river is designed to optimize diffusion.

10) Union Carbide Canada Limited

This plant produces low and high density polyethylene, the former by a high pressure process. Waste flows are low, typically 2273 cubic meters per day, and are essentially uncontaminated. The plant was in the process of being brought on-line at the time of this study and was not sampled; neither were TOC values measured.

11) Allied Chemical Canada Limited

The major product of this plant was toluene di-isocyanate for use in various polyurethane formulations. Wastes were discharged to a single sewer, relevant data being given in Table A13. The plant was closed in December 1978, and later dismantled.

12) Beker Industries of Canada Limited

This plant produced ammonia for use in fertilizers by fixation of atmospheric nitrogen. Discharge to the river occurred via two sewers: one handling process waste water (API); the other used cooling water. Relevant data are supplied in Table A14.

This plant was not operational in 1968: later major concerns were with the potential for ammonia loss. The plant was shut down in November 1977, and is not expected to operate again.

13) Canadian Industries Limited

The CIL plant, again, produces ammonia and fertilizers. Discharge to the river occurs via a single sewer, detailed in Table A15.

Problem areas identified in 1968 were ammonia and phosphorus discharges and pH values that occasionally exceeded the OWRC guidelines. The Company has since installed an ion exchange system, for ammonia removal, and has improved its product handling to reduce spillage and subsequent flushing into the surface drainage system. Alarm-type pH and conductivity probes have also been installed to indicate spillage.

In order to facilitate comparison of the various industrial discharges, mean TOC, flow and net loading data are summarized in Table 1. Where intake TOC values were not measured, a value of 4 mg Carbon/litre has been assumed. Other water quality data, less relevant to the organic analyses, are contained in the Biological Report in this series. It must be stressed that these figures are not absolute and are included only for the purpose of comparison with each other and with the organic analytical data presented later. Plant discharges will vary considerably, in both quantity and quality, dependent on many factors: feed stock quality, product priorities, time of year, ambient temperature, etc. These figures

TABLE 1

Summary of Industrial Discharges

	Mean TOC (mg Carbon/L)	Mean Flow (1000 m^3/day)	Mean Net Loading (kg/day)
Imperial Oil Limited (Tables A1 and A2)			
#3 Separator	3.0	61.4	25.8
#9 Separator	8.3	54.6	314.0
#11,12 Separator	5.8	54.6	173.1
Bio-oxidation	26.7	22.7	546.8
Intake	2.6	--	--
TOTAL			1060.0
Esso Chemical Canada Limited (Table A3)			
Pressure Sewer*	34.7	11.4	350.0
Polysar Limited (Tables A4 and A5)			
Township Ditch	5.6	245.5	737.0
54" Sewer	29.6	72.7	1776.6
66" Sewer	24.8	295.5	5762.3
Stereo API	77.1	2.7	193.9
72" Sewer	5.6	18.0	5.4
Intake	5.3	--	--
TOTAL			7812.0

Table 1 cont'd

	Mean TOC (mg Carbon/L)	Mean Flow (1000 m^3/day)	Mean Net Loading (kg/day)
Dow Chemical Canada Limited (Tables A6 and A7)			
42" Sewer	10.2	55.5	382.6
48" Sewer	3.6	67.7	20.3
Acid Tile	12.7	12.3	115.6
54" Sluice	7.3	35.0	140.0
Second Street Sewer	15.8	52.7	658.8
Third Street Sewer	13.6	130.9	1348.3
D.O.E.O.	3.3	100.9	0
Fourth Street Sewer	8.1	288.7	1385.8
Steam Plant Sewer	3.8	17.3	8.7
Intake	3.3	--	--
TOTAL			4060.0
Sunoco Incorporated (Table A8)			
Total Discharge	6.3	68.2	163.7
Intake	3.9	--	--
Shell Canada Limited (Table A9)			
Contaminated Water	5.6	100.0	240.0
Clean Water	3.8	120.9	72.5
Intake	3.2	--	--
TOTAL			313.0
Ethyl Corporation of Canada (Table A10)			
Total Discharge*	5.3	39.3	40.6

Table 1 cont'd

	Mean TOC (mg Carbon/L)	Mean Flow (1000 m^3/day)	Mean Net Loading (kg/day)
DuPont Canada Incorporated (Table A11)			
Total Discharge*	6.3	27.3	62.8
Petrosar Limited (Table A12)			
Total Discharge	7.8	22.7	102.3
Intake	3.3	--	--
Allied Chemical Canada Limited (Table A13)			
Total Discharge	4.2	16.4	-4.9
Intake	4.5	--	--
Beker Industries of Canada Limited (Table A14)			
Cooling Water	3.8	81.8	122.7
API Sewer	6.6	0.9	5.9
Intake	2.3	--	--
TOTAL			128.6
Canadian Industries Limited (Table A15)			
Total Discharge	2.83	322.8	25.8
Intake	2.75	--	--

*Intake TOC not measured, a value of 4 mg carbon/litre has been assumed.

Figures calculated by subtracting mean intake TOC from mean TOC for each sewer and multiplying result by average flow.

highlight this variability. The calculation assumes that no water loss occurs in the plants, i.e. quantity of water taken in equals quantity of water discharged. This is clearly impossible, and water lost as steam and vapor will have an overall concentrating effect resulting in higher TOC values. This effect will, to some extent, be balanced by a similar loss of volatile organics present in the intake water passing through the plant. It is clear from some of the figures that extrapolation of this kind is not always reliable: a striking example is Allied Chemical of Canada Limited, where the net value is negative, indicating the plant removes organic carbon from the water. Nevertheless, comparisons are possible: Table 1, ignoring data for Allied Chemical of Canada Limited, shows that daily net organic carbon discharges range from 0 to 7812.0 kg/day, while individual sewers may range up to 5762.3 kg/day (Polysar 66" Sewer). The figures also demonstrate that the TOC values alone may not reflect the environmental impact of a particular sewer, but that flow is also important. Thus the Polysar 66" Sewer has the highest net daily loading, but the TOC value (mean 24.8) is considerably lower than that of the Polysar Stereo API Sewer (mean 77.1). Furthermore, since the "Blue Book" ("Water Management Goals, Policies, Objectives and Implementation Procedures of the Ministry of the Environment", Ministry of the Environment, November 1978) lists an acceptable TOC of 5 mg Carbon/litre for drinking water, it is clear that many of the discharges (8 out of 29) are essentially clean while 12 more are within a factor of two (i.e. less than 10 mg Carbon/litre). The remaining nine have mean TOC values ranging from 10.2 to 77.1 mg Carbon/litre, and are associated with Imperial Oil Limited(1), Esso Chemical Canada Limited(1), Polysar Limited(3) and Dow Chemical Canada Limited(4).

Since the initiation of this study and first sampling in 1977, the plants of both Beker Industries of Canada Limited and Allied Chemical Canada Limited have ceased operations.

Pollution abatement is a major concern of both the industries and the Ministry of the Environment, and is subject to on-going improvements. Since the 1977 study industrial efforts have concentrated on improving existing facilities, particularly in the areas of pretreatment and equalization prior to bio-treatment. A further major effort has been in the collection and treatment of surface water

runoff. In contrast the industrial analytical facilities have not improved significantly although all sewers now have composite samplers for routine parameter analyses such as TOC, ammonia, suspended solids, etc.

II. Sewage Treatment Plant (STP) Effluents

As mentioned earlier, STP effluents must be regarded as an important secondary source of organics, particularly where there is a possibility of industrial effluents being discharged via the sewage system. Furthermore, the possibility of producing hazardous chlorinated compounds during the water treatment process cannot be excluded (see Discussion and Appendix III).

Data for the six STP's on the Canadian bank of the St. Clair River are presented in Table 2. Sampling was restricted to the three largest plants; Point Edward, Sarnia and Corunna. In addition to their size, the Point Edward and Sarnia plants only employ primary treatment processes and are, therefore, likely to contribute significant organic loadings to the river.

The relative locations of the industrial and STP discharges described in the preceeding sections are shown in Figure 4. There are two areas that require some clarification: both Sarnia STP and Esso Chemical of Canada Limited discharge their effluents in amongst the Imperial Oil Limited sewers, the order (north-south) being: Imperial #3 separator, Imperial #5 separator, Sarnia STP, Esso Chemical Canada Pressure sewer, Imperial #9 separator, Imperial extended outfall (#11, 12 separator and Bio-oxidation). The Township Ditch is immediately upstream of the Polysar complex, and data for this outfall is always reported with Polysar. In addition to receiving used cooling water discharges from Polysar, the ditch, as mentioned earlier, receives other cooling water discharges from Cabot Carbon, Fiberglas of Canada and Monsanto, drainage from a petroleum tank farm and also landfill sites on Scott Road.

III. Water Quality Samples

For the purposes of this report, "samples that indicate river water quality" are samples from sites where water is removed from the river in addition to actual river water samples. Thus, industrial, municipal and private residential water

TABLE 2

Summary of Municipal Waste Treatment Facilities Along the Canadian Side of the St. Clair River

Municipality	Treatment capacity (cubic meters/day)	Type of treatment	Annual Loading (kilograms) BOD_5	Suspended solids	Total phosphorus
Point Edward[a]	2,590	Primary	40,800	31,300	1,700
Sarnia[a]	65,900	Primary	550,000	355,700	10,353
Corunna[a]	1,450	Extended aeration	4,300	3,900	480
Courtright[a]	570	Extended aeration	210	530	110
Sombra[b]	400 (26 acres)	Lagoons	247	1,317	26
Port Lambton[b]	560 (36 acres)	Lagoons	730	3,636	59

[a]1977 data [b]1978 data

All treatment facilities employ phosphorus removal

Lake Huron

Lambton Area Water Supply System

Point Edward

Black River

Sarnia

Port Huron

IMPERIAL OIL ENTERPRISES (4)

MUELLER LTD.

ESSO CHEMICAL CANADA LTD. (1)

TOWNSHIP DITCH ← CABOT CARBON
FIBERGLAS
MONSANTO
POLYSAR

POLYSAR CORPORATION LTD. (4)

DOW CHEMICAL OF CANADA LTD. (9)

SUNOCO INCORPORATED (1)

Talford Creek

Marysville

SHELL CANADA LTD. (2)

ETHYL CORPORATION OF CANADA LTD. (1)
DUPONT OF CANADA LTD. (1)
PETROSAR LTD. (1)

Stag Island

Corunna

UNION CARBIDE CANADA LTD. (1)
ALLIED CHEMICAL CANADA LTD. (1)

Mooretown

Baby Creek

St. Clair

1000 0 5000 10,000 15,000 FEET

1000 0 5000 METERS

St. Clair

Pine River

Courtright

ONTARIO HYDRO LAMBTON GENERATING STATION

Bowens Creek

BEKER INDUSTRIES OF CANADA LTD. (2)

CANADIAN INDUSTRIES LTD.

Clay Creek

Belle River

Marine City

Sombra

Woodtick (Fawn) Island

Murphy Drain

CHINOOK CHEMICAL CORPORATION LTD.

Marsh Creek

Port Lambton

Chenal Ecarte

LEGEND

× – S.T.P. EFFLUENT SAMPLES

\+ – S.T.P.'S NOT SAMPLED

( ) – INDUSTRIAL DISCHARGES – NO. OF OUTFALLS

MINISTRY OF THE ENVIRONMENT

ST. CLAIR RIVER – FIG. 4

INDUSTRIAL AND S.T.P. EFFLUENT SAMPLING SITES

SCALE: AS SHOWN	
DRAWN BY: A.S.	DATE: JUNE, 1980
CHECKED BY:	DRAWING Nº: 9474A

intakes are also included, and the resulting sites, shown in Figure 5, form a broad picture of river water quality. Samples from the Lambton Area Water Supply System are also presented in this section, although the results cannot be taken as indicative of river quality as analytical work was restricted to the finished water which may include artifacts produced in the treatment process. Furthermore, other organics may have been removed during purification.

IV. Samples Indicating River Water Quality

Since both fish and sediments may accumulate certain organics, they can act as long-term indicators of water quality.

The fish sampling program was organized in co-operation with the Ministry of Natural Resources, and staff from that Ministry submitted frozen fillets to the Laboratory for analysis. The program started rather late in 1977 (October and November) and temperature differences of the water and effluents (sampled April, May and June) may have affected the results. Fish were obtained from the vicinity of Imperial Oil Limited, Stag Island and the Ontario Hydro outfall. Although fish may be regarded as important indicators of water quality, several important problems and factors must be considered. Fish can be quite difficult to analyze because of interferences from bio-organics, particularly lipids. This is somewhat alleviated by performing analyses for volatile organics although, even then, large quantities of aliphatic hydrocarbons frequently mask compounds of greater interest. Factors affecting data interpretation include fish behaviour, position in food chain, habitat, although age, size and related bio-accumulation data are important. During the planning of this study, much emphasis was placed on the fish analyses and considerable thought was given to the above factors. In practice there was little variation in the species caught, which imposed limitations on the study as initially planned.

Bottom sediments, as mentioned above, can be good indicators of water quality and, in many cases, act as important integrators of the pollutant concentrations. All sediments examined for organics contained large quantities of aliphatic hydrocarbons and because of interferences from these compounds detailed analyses were not possible. It was, however, possible to obtain polychlorinated biphenyl (PCB) data, which is included here for the sake of completeness, although

discussion of the results is contained in the biological report. Sediment samples were obtained from two sets of sites: river sites and industrial sites. The former, shown in Figure 6, were chosen to indicate overall river quality, while the industrial sites, Figure 7, were selected for their proximity to industrial outfalls. Figure 7 also indicates the sites of sampling conducted in 1975.

V. Other Samples

In addition to the samples and sites bearing directly on the St. Clair River, detailed above, a variety of samples were obtained from areas adjacent to the river or areas where pollutants arising from the St. Clair may be important. These were:

STP Effluents

Wallaceburg - ultimately discharging to the river and Lake St. Clair (see Figure 2)

Little River (Windsor) - discharging to the Detroit River

West Windsor - discharging to the Detroit River

WTP Water Samples

Walpole Island - water obtained from Lake St. Clair (see Figure 2)

A. J. Brian Pumping Station (Windsor)

Fish

Lake Huron - Blue Point South, close to the St. Clair River

Lake St. Clair (see Figure 1)
- Mitchell's Bay
- Puce
- Tremblay Creek

Routine Monitoring Data - WTP's

Tilbury North
Windsor
Amherstburg

Analytical results for these samples are presented immediately following the St. Clair results proper.

Lake Huron

Lambton Area Water Supply System

Point Edward

Black River

Sarnia

Port Huron

IMPERIAL OIL ENTERPRISES (4)
MUELLER LTD.
ESSO CHEMICAL CANADA LTD. (1)
TOWNSHIP DITCH ← CABOT CARBON, FIBERGLAS, MONSANTO, POLYSAR
POLYSAR CORPORATION LTD. (4)

DOW CHEMICAL OF CANADA LTD. (9)

SUNOCO INCORPORATED (1)

Talford Creek

Marysville

SHELL CANADA LTD. (2)

ETHYL CORPORATION OF CANADA LTD. (1)
DUPONT OF CANADA LTD. (1)
PETROSAR LTD. (1)

Stag Island

Corunna

UNION CARBIDE CANADA LTD. (1)
ALLIED CHEMICAL CANADA LTD. (1)

Mooretown

Baby Creek

St. Clair

1000 0 5000 10,000 15,000 FEET

1000 0 5000 METERS

St. Clair

Pine River

Courtright

ONTARIO HYDRO LAMBTON GENERATING STATION

Bowens Creek

BEKER INDUSTRIES OF CANADA LTD. (2)

CANADIAN INDUSTRIES LTD.

Clay Creek

Belle River

Marine City

Sombra

Woodtick (Fawn) Island

Murphy Drain

CHINOOK CHEMICAL CORPORATION LTD.

Marsh Creek

Port Lambton

Chenal Ecarte

LEGEND

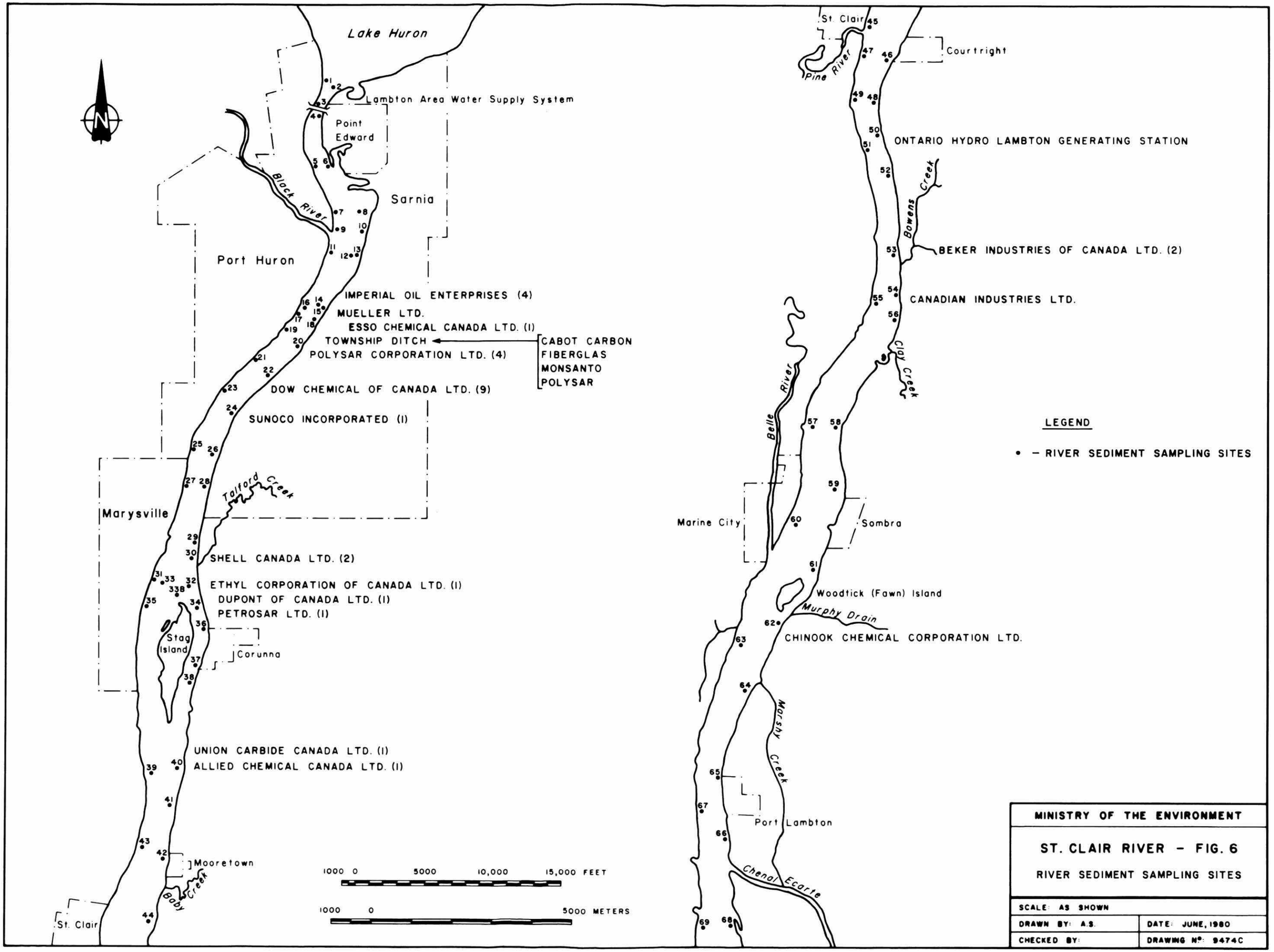
- o – WATER TREATMENT PLANT
- * – RIVER WATER
- □ – INTAKE WATER
- ● – PRIVATE RESIDENCES

MINISTRY OF THE ENVIRONMENT

ST. CLAIR RIVER – FIG. 5

WATER QUALITY SAMPLING SITES

SCALE: AS SHOWN	
DRAWN BY: A.S.	DATE: JUNE, 1980
CHECKED BY:	DRAWING Nº: 94748


Lake Huron
Lambton Area Water Supply System
Point Edward
Sarnia
Black River
Port Huron
IMPERIAL OIL ENTERPRISES (4)
MUELLER LTD.
ESSO CHEMICAL CANADA LTD. (1)
TOWNSHIP DITCH
CABOT CARBON
FIBERGLAS
MONSANTO
POLYSAR
POLYSAR CORPORATION LTD. (4)
DOW CHEMICAL OF CANADA LTD. (9)
SUNOCO INCORPORATED (1)
Talford Creek
Marysville
SHELL CANADA LTD. (2)
ETHYL CORPORATION OF CANADA LTD. (1)
DUPONT OF CANADA LTD. (1)
PETROSAR LTD. (1)
Stag Island
Corunna
UNION CARBIDE CANADA LTD. (1)
ALLIED CHEMICAL CANADA LTD. (1)
Mooretown
Baby Creek
St. Clair
1000 0 5000 10,000 15,000 FEET
1000 0 5000 METERS
St. Clair
Courtright
Pine River
ONTARIO HYDRO LAMBTON GENERATING STATION
Bowens Creek
BEKER INDUSTRIES OF CANADA LTD. (2)
CANADIAN INDUSTRIES LTD.
Clay Creek
Belle River
Marine City
Sombra
Woodtick (Fawn) Island
Murphy Drain
CHINOOK CHEMICAL CORPORATION LTD.
Marshy Creek
Port Lambton
Chenal Ecarte
LEGEND
• – RIVER SEDIMENT SAMPLING SITES
MINISTRY OF THE ENVIRONMENT
ST. CLAIR RIVER – FIG. 6
RIVER SEDIMENT SAMPLING SITES
SCALE: AS SHOWN
DRAWN BY: A.S.
DATE: JUNE, 1980
CHECKED BY:
DRAWING Nº: 9474C

Lake Huron

Lambton Area Water Supply System

Point Edward

Sarnia

Black River

Port Huron

1 IMPERIAL OIL ENTERPRISES (4)
2 MUELLER LTD.
3 ESSO CHEMICAL CANADA LTD. (1)
4 TOWNSHIP DITCH ← CABOT CARBON, FIBERGLAS, MONSANTO, POLYSAR
5 POLYSAR CORPORATION LTD. (4)
6 DOW CHEMICAL OF CANADA LTD. (9)
7 SUNOCO INCORPORATED (1)

Talford Creek

Marysville

8 SHELL CANADA LTD. (2)
9 ETHYL CORPORATION OF CANADA LTD. (1)
10 DUPONT OF CANADA LTD. (1)
11 PETROSAR LTD. (1)

Stag Island

Corunna

12 UNION CARBIDE CANADA LTD. (1)
13 ALLIED CHEMICAL CANADA LTD. (1)

Mooretown

Baby Creek

St. Clair

1000 0 5000 10,000 15,000 FEET

1000 0 5000 METERS

St. Clair

Pine River

Courtright

14 ONTARIO HYDRO LAMBTON GENERATING STATION

Bowens Creek

15 BEKER INDUSTRIES OF CANADA LTD. (2)
16 CANADIAN INDUSTRIES LTD.

Clay Creek

Belle River

Marine City

Sombra

Woodtick (Fawn) Island

Murphy Drain

17 CHINOOK CHEMICAL CORPORATION LTD.

Morsby Creek

Port Lambton

Chenal Ecarte

LEGEND

• – INDUSTRIAL SEDIMENT SAMPLING SITES

MINISTRY OF THE ENVIRONMENT

ST. CLAIR RIVER – FIG. 7

INDUSTRIAL SEDIMENT SAMPLING SITES

SCALE: AS SHOWN	
DRAWN BY: A.S.	DATE: JUNE, 1980
CHECKED BY:	DRAWING Nº: 9474D

SAMPLING PROGRAM

Since data from the preliminary (1975-76) organics survey is included with the analytical results, the samples collected are described here along with those for the extended (1977) study.

The preliminary study concentrated on industrial sites, although some sediments were also examined. The industrial samples were from both final effluents, i.e. discharges to the river, and a variety of in-plant process streams. The only samples that may be used to compare river water quality were those collected from industrial intake waters. All samples used in the preliminary study of 1975-76 were grab samples.

In contrast, a far wider range of samples, as noted previously, were collected for the 1977 study. The industrial samples were limited to intakes and discharges to the river, but STP, WTP, private residence, fish and sediment samples were also collected. In order to minimize the effects of discharge variations (both quality and quantity) the majority of industrial samples were 24-hour composites.

Sampling for the extended study proceeded in three phases. Initially, during May to August 1977, samples were collected from all sites. But as the analytical work proceeded, it became clear that there were large variations in organic concentrations from sample to sample, particularly in the industrial effluents, and four possible reasons were identified:

i) Actual effluent variations.

ii) Awareness of the sampling program by the industries concerned, with possible strict, temporary effluent control.

iii) Variation in sample collection or handling procedures, i.e. variable amounts of headspace and storage periods.

iv) Variations in analytical procedure or instrument performance.

In view of the scale and complexity of industrial operations on the St. Clair River, point i) is thought to be highly likely. Point ii) is thought unlikely as industrial operating schedules are normally arranged well in advance, although it is possible that operations which would give unreasonably high levels, i.e. reactor cleaning, could be temporarily postponed during sampling. It is frequently observed that grab samples show higher levels of organics than automatic composites, and this factor appears more important than storage time. Since automatic samples often have large, and variable, amounts of headspace and may be open to atmosphere longer during sampling, it is thought that point iii) may be the major factor. This is also likely to most affect samples with high concentrations of more volatile components. Point iv) is thought unlikely since blanks and standards were analyzed frequently. Effluent variation is also supported by the TOC values, presented under background information, which were obtained independently of the organic analyses. Because of these factors it is believed that many of the results reported here are underestimates.

The sheer volume of samples collected in 1977 necessitated the setting of analytical priorities and, because of concerns over the effluent variations, by no means all samples (six per site) were analyzed. At least one sample was analyzed from each site, but efforts were concentrated on sites known from earlier work to contain large quantities of organics. A re-sampling program was proposed and commenced in the summer of 1978. Grab samples were obtained from four outfalls:

Imperial Oil Limited #9 Separator
Polysar Limited 54" Sewer
Polysar Limited 66" Sewer
Dow Chemical Canada Limited Third Street Sewer

and were collected at various times over a period of several days.

Later in 1978 additional unannounced sampling was performed on the intake waters to Dow Chemical Canada Limited and Polysar Limited and the discharges from Dow's Third Street sewer and Polysar's Stereo API. Composite samples were taken over a 24-hour period with additional grab samples at four hourly intervals. During the sampling period, the Dow Plant experienced an incident that resulted in

the discharge of considerable quantities of organics to the Third Street Sewer before the contingency plans operated (see Table 26, page 62). While the results for these samples cannot, therefore, be taken as representing effluent quality, they do indicate levels of organics that can result from such accidents. Considering the scale of the industrial operations, it would seem reasonable to assume that accidental discharges of this nature are quite frequent.

For the sake of clarity, the industrial effluent sampling program is summarized, for both studies, in Table 3. As shown in the Table many additional in-plant sites were sampled in 1975 but, nevertheless, there is sufficient duplication of sites to permit some comparisons.

The sites for sediment samples collected during the 1975-76 study are described in the Analytical Results section, page 33.

TABLE 3

Summary of Industrial Sampling Sites for the
1975/76 and 1977 St. Clair River Studies

	1975/76	1977	May 1978	Oct. 1978
Imperial Oil Limited				
Intake Water	+	+		
Refinery Filter Influent*	+			
Refinery Filter Effluent*	+			
#3 Separator	+	+		
#9 Separator	+	+	+	
#11 Separator*	+			
#12 Separator*	+			
#11,12 Separator*		+		
Bio-oxidation Unit*	+	+		
Esso Chemical Canada Limited				
Intake Water	+			
Chemical Plant Filter Influent*	+			
Chemical Plant Filter Effluent*	+			
Pressure Sewer		+		
Fiberglas Limited				
Intake Water	+			
Total Discharge	+			
Polysar Limited				
Intake Water	+			+
Township Ditch, above Polysar	+			
Township Ditch	+	+		
54" Sewer	+	+	+	
66" Sewer	+	+	+	
Stereo API	+	+		+
72" Sewer	+	+		

Table 3 cont'd

	1975/76	1977	May 1978	Oct. 1978
Dow Chemical Canada Limited				
42" Sewer	+	+		
48" Sewer	+	+		
Acid Tile	+	+		
54" Sluice	+	+		
Second Street Sewer	+	+		
North Intake	+	+		+
Third Street Sewer	+	+	+	+
D.O.E.O.	+	+		
Fourth Street Sewer	+	+		
Steam Plant	+	+		
South Intake	+			
Sunoco Incorporated				
Intake Water	+	+		
Total Discharge	+	+		
Shell Canada Limited				
Intake Water	+	+		
Bio-treater Influent*	+			
Bio-treater Effluent*	+			
DAF Effluent*	+			
Potentially Oily Water*	+			
Clean (cooling) Water	+	+		
Contaminated (combined) Water	+	+		
Ethyl Corporation of Canada Limited				
Intake Water	+			
Hydramation Filter Effluent*	+			
Hydrolysis Pit Effluent*	+			
Total Plant Effluent	+	+		
DuPont Canada Incorporated				
Intake Water	+			
Plant Effluent	+	+,		

Table 3 cont'd

	1975/76	1977	May 1978	Oct. 1978
Allied Chemical Canada				
Intake	+	+		
Total Discharge	+	+		
Beker Industries of Canada Limited				
Intake	+	+		
Cooling Water	+	+		
API Sewer	+	+		
Canadian Industries Limited				
Intake Water	+	+		
Phosphate Ditch*	+			
Urea Plant Effluent*	+			
Nitrate Sewer*	+			
Total Effluent	+	+		

* Indicates in-plant sample: these are samples collected from points in the process or treatment streams and are further treated or combined with other streams before discharge to the river.

+ Indicates sampling during the period shown.

ANALYTICAL PROCEDURES

During the 1975-76 study, samples were examined by a variety of techniques. In order to reduce the GC/MS loading, samples were first extracted with cyclohexane at pH 7, pH 1 and pH 11 and screened by injecting 5 ul aliquots of the concentrated extracts onto a GC equipped with a flame ionization detector (FID) and a 6' x 1/8" glass column containing 3% UCW-98 on Chromosorb W. The temperature was programmed from 60 to 200°C at 10°C/min. Samples showing significant levels of organic compounds were then analyzed further. Compound identification was performed using GC/MS and a purge and trap technique (described later). This analysis was essentially qualitative although the concentrations of some components (chloroethane, dichloroethane, trichloroethane, tetrachloroethane, tetrachloroethylene, dichloropropane, tetrachloropropane, hexachlorobutadiene, butadiene, diethylbenzene, dimethyldiethylbenzene and diphenyl ether) were estimated from the response of a FID which received part of the GC effluent. Gas chromatographic conditions were as described previously.

Following compound identification, appropriate GC-only analyses for quantitation were performed on replicate samples as follows:

a) Volatile Organohalides

Chloroform, dichlorobromomethane, dibromochloromethane, carbon tetrachloride and trichloroethylene were analyzed by the direct aqueous injection of 9 uL aliquots to a GC equipped with an electron capture detector (ECD). This method is detailed in an earlier report ("Organics in Ontario Drinking Waters, Part I. The Occurrence and Determination of Free and Total Potential Haloforms" by A. A. Nicholson and O. Meresz, Ministry of the Environment, 1976). The detection limit of this method is 0.5 ppb for chloroform. Routine monitoring data (see Analytical Results, Section v "Other Samples") was obtained by this method.

b) Vinyl Chloride

Samples collected separately in 20 ml hypo-vials, were subjected to headspace analysis for vinyl chloride. Headspace gases were injected onto a 7' x 1/8" 0.4% Carbowax 400 column operated isothermally at 100°C. The detection limit was 1 ug/litre (1 ppb).

c) Alcohols

Direct aqueous injection using a 6' x 1/8" Poropak column programmed from 90° to 250°C at 8°C/min was employed to quantitate alcohols. A variety of calibration curves were determined but only ethanol, i-propanol and t-butanol were observed in real samples. The detection limit was 1 mg/litre (1 ppm).

d) Aromatic Hydrocarbons

Quantitation for benzene, toluene, xylene, ethylbenzene and styrene was performed by extracting a 900 ml aliquot with 1.0 ml hexane followed by analysis on a 22' x 1/8" 5% Bentone-34/5% DIDP column operated isothermally at 125°C. The detection limit with a flame ionization detector was 1 mg/litre (1 ppm).

Analyses of sediments was largely restricted to determination of the chloroform solvent extractables although GC/MS analyses, using the purge technique, were performed on some samples.

Analytical methodology for 1977 was restricted to GC/MS analyses for volatile organics using the same purge and trap procedure as in 1975, described below, but employed quantitatively. This obviated the need for separate GC-only quantitation, resulted in improved detection limits (0.05 to 0.1 ug/litre for most compounds) and increased the range of compounds that could be quantitated, but did necessitate long storage of many samples.

The apparatus used for purging is illustrated in Figure 8. Samples, generally 1 litre, were placed in the specially constructed glass purge vessel which had been previously thoroughly cleaned with chromic acid and organic-free water. The vessel contained a glass frit and a tube to allow the purge gas to be admitted below the frit, dispersed and passed through the sample. Dispersion was aided by magnetic stirring. The vessel was placed in a water bath held at 90°C and purged with dry nitrogen for 30 minutes. Heating permitted several higher molecular weight components, for example, ethyl and higher substituted benzenes, naphthalene and substituted naphthalenes and dichlorobenzene to be purged and analyzed. Low molecular weight is not, of course, the only criterion for successful purging. Thus highly polar compounds such as phenols, acids, amines, glycols, etc. do not

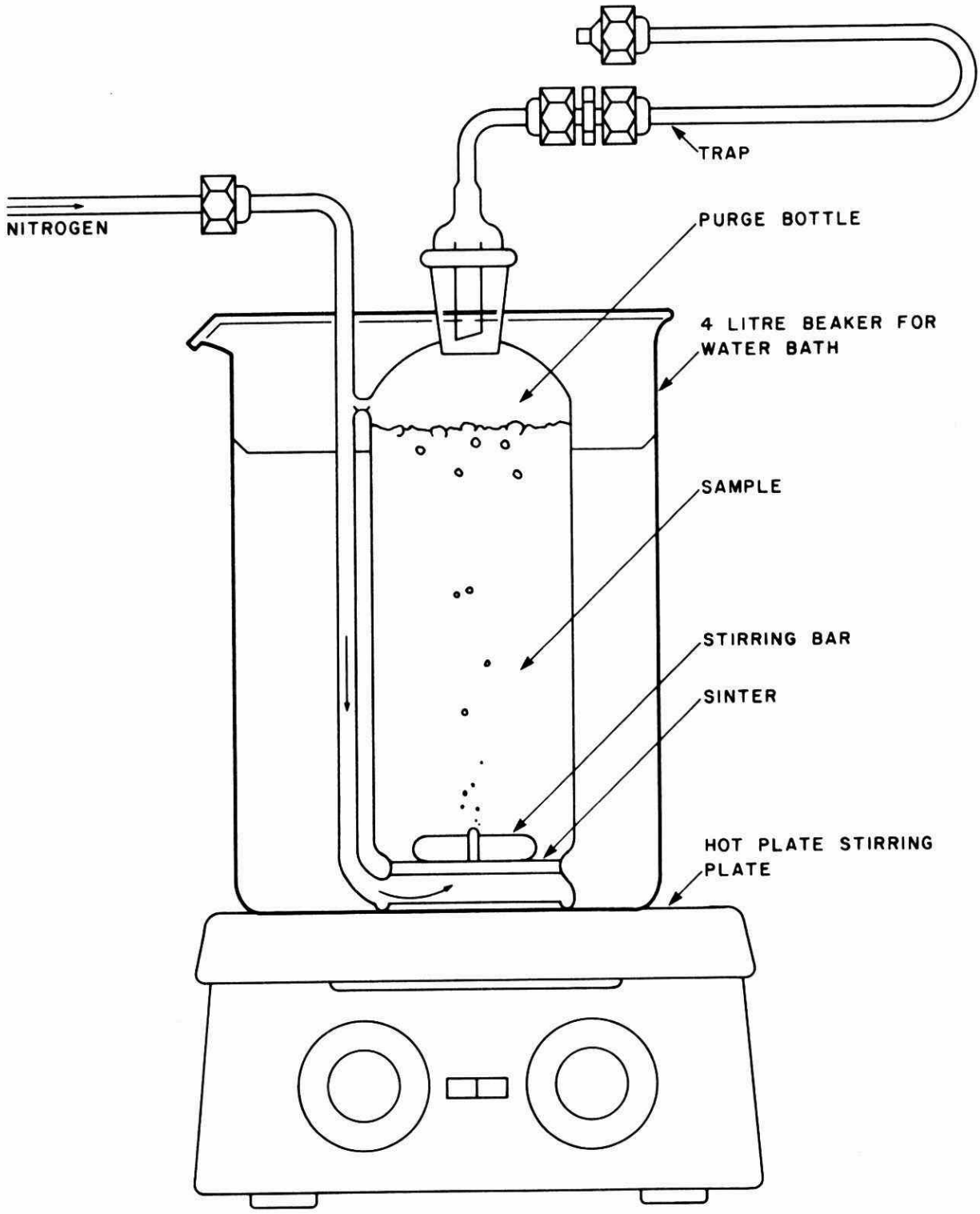


FIGURE 8 - SCHEMATIC OF PURGING APPARATUS

purge well, if at all, and would not have been detected in this study. The nitrogen and volatile organics emerging from the vessel passed through a Stainless Steel U-tube containing Tenax GC and Dexsil 300, which trapped the organics. Following purging, the trap was transferred to the Gas Chromatograph of a GC/MS system and thermally desorbed onto the analytical column as the oven temperature increased. In early work a very short (1 foot) Chromosorb 101 column was used. This produced short runs, but showed poor resolution resulting in some components being missed and causing quantitation problems, because of overlapping peaks. 1977 samples were analyzed using a 12 foot Tenax GC column, with far better results. The temperature program used was 60-200°C at 10°C/minute. The column effluent was split between a flame ionization detector (FID) and the mass spectrometer. Positive identification of the organics observed was obtained by examining the mass spectra while quantitation was achieved from the FID output using an external standard, that is, comparison of FID responses for the unknown concentrations with those from standards. Recovery rates were measured by comparing FID responses from purged standard solutions against responses from the solution injected directly into the GC.

A single set of samples (Table 42) were taken in 1980 to clarify some earlier results from the Lambton Water Supply System (Table 41). These were quantitated by MS, rather than FID, response following on-going development to improve reliability and precision.

During most of the analyses reported here, the following equipment was used:

Gas Chromatograph: Hewlett-Packard 7620A
Mass Spectrometer: AEI (Kratos) MS30

In some later analyses, the following was employed:

Gas Chromatograph: Varian 2740
Mass Spectrometer: DuPont Instruments 21-491BR

In both systems, GC/MS interfacing was via a jet separator and the MS output was connected to an AEI (Kratos) Datasystem, model DS50 (later DS50S), for acquisition of the mass spectra and assistance with the interpretation of results. A

Shimadzu integrator was used to provide area measurements of the FID response for quantitation.

Fish and sediment samples were analyzed in a similar fashion, except that a weighed portion of sample was added to one litre of organic-free water in the purge vessel. Frequent analyses of organic-free water blanks were performed.

ANALYTICAL RESULTS

In the following tables data is presented in the five groups discussed previously in the section on background information, viz:

i) Industrial Effluents
ii) Sewage Treatment Plant Effluents
iii) Samples Indicating Water Quality
iv) Samples Dependent on Water Quality
v) Other Samples

"Other Samples" are samples from sites not immediately on the St. Clair River. Within each group, results are presented for sites taken in order from North to South.

Under the conditions of these analyses, i.e. identification/confirmation by Mass Spectrometry with quantitation by Gas Chromatography, accurate quantitation can generally be performed in the range 100 ng/litre (100 ppt) to 1 mg/litre (1 ppm). Identification was often possible outside this range, however, both at trace (50-100 ppt) levels and at concentrations in excess of 1 ppm. In the following data these situations are denoted + and M respectively.

i) Industrial Effluents

Analytical results for the industrial effluents are presented in the following Tables. They are arranged as follows:

Site(s)	Date	Table
Imperial Oil Limited		
#3 Separator	1975, 1977	4
#9 Separator	1975, 1977	5
#9 Separator	May 1978	6

Site(s)	Date	Table
#11 and #12 Separator	1975, 1977	7
Bio-oxidation Unit	1977	8
Esso Chemical Canada Limited		
Pressure Sewer	1977	9
Fiberglas Canada Limited		
Total Discharge	1975	10
Polysar Limited		
Township Ditch	1975, 1977	11
54" Sewer	1975, 1977	12
54" Sewer	May, 1978	13
66" Sewer	1975, 1977	14
66" Sewer	May 1978	15
Stereo API	1975, 1977	16
Stereo API	October 1978	17
72" Sewer	1975, 1977	18
Dow Chemical Canada Limited		
42" Sewer	1975, 1977	19
48" Sewer	1975, 1977	20
Acid Tile	1975, 1977	21
54" Sluice	1975, 1977	22
Second Street	1975, 1977	23
Third Street	1975, 1977	24
Third Street	May 1978	25
Third Street	October 1978	26
D.O.E.O.	1975, 1977	27
Fourth Street	1975, 1977	28
Steam Plant	1975, 1977	29

Site(s)	Date	Table
Sunoco Incorporated		
Total Discharge	1975, 1977	30
Shell Canada Limited		
Clean Water	1975, 1977	31
Contaminated Water	1975, 1977	32
Ethyl Corporation of Canada		
Total Discharge	1975, 1977	33
DuPont Canada Incorporated		
Total Discharge	1977	34
Allied Chemical Canada Limited		
Total Discharge	1975, 1977	35
Beker Industries of Canada Limited		
Cooling Water and API Sewer	1977	36
Canadian Industries Limited		
Total Discharge	1975, 1977	37

ii) Sewage Treatment Plant Effluents

The following tables present the analytical data for STP effluents:

Site(s)	Date	Table
Point Edward. Final Effluent	1977	38
Sarnia. Raw Sewage and Final Effluent	1977	39
Corunna. Final Effluent	1977	40

iii) Samples Indicating River Water Quality

Analytical data for river water Municipal and Private water supplies and industrial service water samples are presented in the following Tables. They are arranged in the following order:

Site(s)	Date	Table
Lambton Water Supply System		
Finished Water	1977	41
Raw and Finished Water	1980	42
River Water. Blue Water Bridge	1977	43
Imperial Oil Limited		
Intake Water	1975, 1977	44
Polysar Limited. Intake Water	1975, 1977, 1978	45
Dow Chemical Canada Limited		
North Intake	1975, 1977, 1978	46
South Intake	1975	47
River Water. Dow Chemical/ Sunoco Fence Line	1977	48
Sunoco Incorporated		
Intake Water	1975, 1977	49
River Water. Sunoco Below Dock	1978	50
Shell Canada Limited		
Intake Water	1975, 1977	51

iii) Samples Indicating River Water Quality, continued

Site(s)	Date	Table
River Water. Talford Creek	1978	52
Allied Chemical Canada Limited Intake Water	1975, 1977	53
Private Residence Water Supplies St. Clair Parkway	1977	54
Beker Industries of Canada Limited Intake Water	1975, 1977	55
Canadian Industries Limited Intake Water	1975, 1977	56
River Water. Sombra Ferry Dock	1977	57

i) Two samples from different dates

iv) Samples Dependent on Water Quality

Analytical results for fish and bottom sediment samples presented in the following Tables, and arranged as follows:

Site(s)	Date	Table
a) Fish		
Below Imperial Oil	1977	58
Near Stag Island	1977	59
Lambton Power Station Outfall	1977	60

iv) Samples Dependent on Water Quality, continued

b) Bottom Sediments

Various[i)]	1975	61
Various[ii)]	1975	62
River Stations[iii)]	1977	63
Industrial Stations[iii)]	1977	64

i) Solvent extractabe data

ii) Qualitative GC/MS by purge and trap

iii) PCB data

v) Other Samples

Data for STP effluents, WTP waters and fish not directly influencing, or influenced by, the St. Clair River are presented in the following tables:

Site(s)	Date	Table
Wallaceburg STP. Raw sewage and final effluent	1977	65
Little River STP. Raw sewage and final effluent	1977	66
West Windsor STP. Raw sewage and final effluent	1977	67
Walpole Island WTP Finished Water	1977	68
A. J. Brian Pumping Station Raw and Finished Water	1977	69

v) Other Samples, continued

Site(s)	Date	Table
Fish from Lake Huron and Lake St. Clair	1977	70
Tilbury North Township WTP Finished Water	1978, 1979	71
Windsor WTP Finished Water	1977, 1978	72
Amherstburg WTP Finished Water	1977, 1978, 1979	73

TABLE 4

Imperial Oil Limited
#3 Separator - 1975 and 1977

	1975 Grab	May 10, 1977 Composite
Methylene Chloride	--	3
Chloroform	NQ	--
Benzene	--	0.1
Toluene	NQ	--
Xylene	NQ	--
TOC (May 10, 1977) mg Carbon/litre	NQ	4.5

All values in ug/litre (ppb)

NQ detected not quantitated
- not detected

TABLE 5

Imperial Oil Limited
#9 Separator - 1975 and 1977

	1975 Grab	May 10, 1977 Composite
Methylene Chloride	--	2
Chloroform	NQ	--
Carbon tetrachloride	--	2
Toluene	NQ	--
Xylene	NQ	--
TOC (May 10, 1977) mg Carbon/litre	NQ	8

All values in ug/litre (ppb)

NQ detected not quantitated
- not detected

TABLE 6

Imperial Oil Limited
#9 Separator - May 1978

	May 25			May 26
	Noon	4 p.m.	8 p.m.	8 a.m.
Methylene Chloride	1	5	26	142
Chloroform	-	-	+	+
1,1 dichloroethane	-	+	-	-
Trichloroethylene	+	+	-	+
Toluene	+	+	-	+
Xylene	-	+	-	+

All Grab Samples
All values in ug/litre (ppb)

\+ trace (0.05 - 0.1 ppb)
\- not detected

TABLE 7

Imperial Oil Limited
#11 and #12[i] Separator - 1975 and 1977

	1975 Grab		1977 Composite
	#11	#12	#11,12 Separator
Methylene chloride	-	-	8
Chloroform	NQ	-	-
Cyclohexane	-	NQ	-
Toluene	NQ	NQ	-
Xylene	NQ	NQ[ii]	-
TOC (May 10, 1977) mg Carbon/litre	NQ	NQ	6

All values in ug/litre (ppb)

NQ detected not quantitated
- not detected

i) In 1975/6 sewers were sampled separately. In 1977 combined effluent was sampled prior to mixing with Bio-oxidation effluent

ii) or ethylbenzene

TABLE 8

Imperial Oil Limited
Bio-oxidation Unit

	May 10, 1977 Composite
Chloroform	3
Benzene	86
Toluene	+
Petroleum Hydrocarbons	NQ
TOC, mg Carbon/litre	13.5

All values in ug/litre (ppb)

+ trace (0.05 - 0.1 ppb)
NQ detected not quantitated

TABLE 9

Esso Chemical Canada Limited

Pressure Sewer

1977

	May 10	May 31	June 21	July 12
Benzene	72	-	20	59
Toluene	176	-	39	1000
Xylenes	30	3	98	7
Styrene	30	-	-	-
Cumene/ethyltoluene	30	0.2	59	-
Trimethylbenzenes	15	-	-	517
Propylbenzene	-	-	95	-
Diethylbenzenes	-	-	40	-
Methylstyrene	-	-	NQ	-
Triethylbenzenes	-	+	-	-
Naphthalene	M	3	24	+
Methylnaphthalene	M	6	3000	+
Dimethylnaphthalene	-	-	-	NQ
Indane	-	-	-	+
Methylindane	-	+	-	-
TOC (mg Carbon/litre)	35.5	37.5	15.5	22.5

* Grab Samples

All values in ug/litre (ppb)

NQ detected not quantitated

+ trace (0.05 - 0.1 ppb)

- not detected

M ppm level

TABLE 10

Fiberglas Canada Limited
Total Discharge 1975

Vinyl Chloride	32
Dichloroethane	NQ i)
Trichloroethane	NQ i)
Trichloroethylene	2
Hexachlorobutadiene	NQ i)
Toluene	NQ

All values in ug/litre (ppb)

NQ detected not quantitated
i) estimated as 10 - 100 ppb

TABLE 11

Polysar Limited
Township Ditch[i] 1975 and 1977

	1975		1977 Composite		
	Above*	Below*	April 18*	May 10	Aug. 30
Methylene Chloride	-	-	-	-	12
Chloroform	2	-	+	+	-
Carbon Tetrachloride	-	-	-	+	-
Chloroethane	NQ [ii]	-	-	-	-
Dichloroethanes	NQ [ii]	-	-	-	-
Tetrachloroethane	NQ [ii]	NQ [ii]	-	-	-
Hexachloroethane	-	-	+	-	-
Trichloroethylene	18	-	-	-	-
Tetrachloroethylene	-	-	+	-	0.4
Hexachlorobutadiene	NQ [ii]	-	+	-	-
Benzene	-	NQ [ii]	-	+	-
Vinyl Chloride	215	10	-	-	-
TOC (mg Carbon/litre)	NQ	NQ	NQ	5.5	5

All values in ug/litre (ppb)
- not detected
+ trace (0.05 - 0.1 ppb)
NQ not quantitated
* Grab Sample

i) 1975/76 sampling was conducted at two points: above and below Polysar. 1977 sampling was below Polysar only.

ii) estimated to be 10 - 100 ppb.

TABLE 12

Polysar Limited. 54" Sewer

	1975*	1977		
		April 18*	May 10	June 21
Chloroform	-	-	+	-
Trichloroethylene	NQ	-	-	-
Methylethylketone	NQ	-	-	-
Propanol	NQ	-	-	-
t-Butanol	376 ppm	-	-	+
But-2-en-1-ol	NQ	-	-	-
Vinyl Chloride	172	-	-	-
Aliphatic hydrocarbons	-	+	+	+
TOC (mg Carbon/litre)	NQ	NQ	36	27

Except where noted all values in ug/litre (ppb)

* Grab Samples

\- not detected

\+ trace (0.05 - 0.1 ppb)

NQ detected not quantitated

TABLE 13

Polysar Limited. 54" Sewer

	May 24, 1978	May 25, 1978		May 26, 1978	
	8 a.m.	8 a.m.	8 p.m.	8 a.m.	Noon
Methylene Chloride	288	-	-	-	-
Butadiene	+	+	-	-	-
Butene	+	-	-	-	-
t-butanol	+	16	194	440	+
Di-isobutylene	+	-	-	+	-
Tri-isobutylene	-	-	-	+	-
Vinylcyclohexene	-	-	-	+	-
Benzene	-	-	-	-	+
Toluene	-	+	0.2	+	-
C_2-alkylbenzene	-	-	4	+	-
C_3-alkylbenzene	-	-	3	+	+
C_4-alkylbenzene	-	-	5	+	-
Diethylxylene	-	-	2	+	-
Ethylstyrene	-	-	+	+	-
C_6-alkylbenzene	-	-	0.2	+	-
Aliphatic Hydrocarbons	-	+	+	-	-

All Grab Samples

All concentrations in ppb (ug/litre)

+ trace (0.05 - 0.1 ppb)

- not detected

TABLE 14

Polysar Limited. 66" Sewer - 1975 & 1977

	1975*	1977		
		April 18*	May 10	July 12
Acetone	NQ	-	-	-
Methylene chloride	-	-	+	+
Chloroform	55	+	+	-
Butadiene	-	NQ	-	-
Benzene	-	+	-	-
Xylenes	NQ[i)]	+	-	-
Trimethylbenzene	-	+	-	-
Cumene	NQ	-	-	-
Diethylbenzene	NQ	+	-	-
Naphthalene	-	+	18	-
Methylnaphthalene	-	-	100	-
Vinyl Chloride	30	-	-	-
Carbon disulphide	NQ	-	-	-
TOC (mg Carbon/litre)	NQ	-	23	30

All values in ug/litre (ppb)

+ trace (0.05 - 0.1 ppb)

- not detected

NQ detected not quantitated

* Grab sample

i) or ethylbenzene

TABLE 15

Polysar Limited. 66" Sewer

1978

	May 24	May 25			May 26	
	5 pm	Noon	4 pm	8 pm	8 am	Noon
Methylene chloride	100	-	+	39	-	123
Chloroform	+	4	+	5	+	5
Dichloroethane-1,1	-	-	-	-	+	-
Dichloroethane-1,2	12	-	-	-	-	-
Dichloropropane	3	-	-	-	-	-
Dichloroethylene	1	-	-	-	-	-
Butene	+	+	-	-	+	-
Butadiene	+	+	+	+	+	+
t-Butanol	*	60	-	-	104	-
Di-isobutylene	-	+	+	-	+	+
Vinylcyclohexene	-	+	-	-	-	-
Benzene	+	-	+	-	-	-
Xylene(s) or Ethylbenzene	-	23	-	-	-	-
Trimethylbenzene or Ethyltoluene	-	44	-	-	-	-
Diethylbenzene	-	47	-	-	-	-
Acetophenone	-	+	+	-	-	-
Hexamethylbenzene	-	+	+	-	+	-
Di-isopropylbenzene	-	+	+	-	-	-
Trimethylethylbenzene	-	+	+	-	-	-
Aliphatic Hydrocarbons	+	-	+	+	-	+

All Grab Samples

* detected under unresolved GC peak

All concentrations in ug/litre (ppb)

+ trace (0.05 - 0.1 ppb) - not detected

TABLE 16

Polysar Limited
Stereo API - 1975 and 1977

	1975*	1977		
		April 18*	May 10	July 12
Acetone	NQ	-	-	-
Ethanol	47 ppm	-	-	-
Butadiene	NQ[i)]	NQ	-	-
Buten-3-yne	NQ	-	-	-
Benzene	149 ppm	+	+	41
Toluene	12 ppm	-	+	-
Xylene(s)	5 ppm	-	+	-
Cumene	NQ	+	-	-
Trimethylbenzene(s)	-	+	-	-
Diethylbenzene(s)	-	+	-	-
Styrene	NQ	+	+	-
Methylstyrene	-	+	-	-
Naphthalene	NQ[ii)]	-	-	-
Methylnaphthalene	NQ	-	-	-
Vinyl Chloride	384	-	-	-
TOC (mg Carbon/litre)	NQ	NQ	90	77

Except where noted, all figures in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)
NQ detected not quantitated
* Grab sample

i) estimated as 10 - 100 ppb
ii) or divinyl benzene

TABLE 17

Polysar Limited
Stereo API - 1978

Date and Time	Benzene (ppm)
October 18, Noon	9
October 18, Noon*	55
October 18, 3 p.m.	68
October 18, 4 p.m.*	73
October 18, 6 p.m.	40
October 18, 8:20 p.m.*	76
October 18, 9 p.m.	55
October 18, Midnight*	92
October 18, Midnight	105
October 19, 2 a.m.	65
October 19, 4:20 a.m.*	93
Octboer 19, 6 a.m.	64
October 19, 8 a.m.	94
October 19, 9 a.m.	104

Note: samples marked * are grab; others were sampled automatically

Quantitation was by Direct Aqueous Injection. Butadiene was present in all samples; butene and methylene chloride were detected in grab samples.

TABLE 18

Polysar Limited
72" Sewer - 1975 and 1977

	1975*	1977	
		April 18*	May 31
Methylene chloride	-	-	124
Trichloroethylene	-	NQ	NQ
i-Propanol	4 ppm	-	-
t-Butanol	7ppm	-	-
Butane-1,4-diol	-	NQ	-
Butadiene	-	NQ	-
Chloropropene	NQ	-	-
Vinyl chloride	4	-	-
TOC (mg Carbon/litre)	NQ	NQ	6

Except where noted, values in ug/litre (ppb)

- not detected

NQ detected not quantitated

* Grab sample

TABLE 19

Dow Chemical Canada Limited
42" Sewer - 1975 and 1977

	1975*	1977	
		April 18*	May 10
Methylene chloride	NQ	+	+
Carbon tetrachloride	110	+	-
Chloroethane	NQ	-	-
Dichloroethane	NQ	+	+
Trichloroethane	-	-	+
Tetrachloroethane	NQ	+	+
Hexachloroethane	NQ	-	-
Dichloroethylene	NQ	-	-
Trichloroethylene	102	+	+
Tetrachloroethylene	NQ	+	-
Dichloropropane	NQ	+	+
Hexachlorobutadiene	-	NQ	-
Benzene	NQ	-	-
Xylene(s)	NQ[i)]	-	-
Diethylbenzene(s)	-	NQ	-
Vinyl Chloride	1	-	-
TOC (mg Carbon/litre)	NQ	NQ	6

All values in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)
NQ detected not quantitated
* Grab sample
i) estimated as 10 - 100 ppb

TABLE 20

Dow Chemical Canada Limited
48" Sewer - 1975 and 1977

	1975*	1977	
		April 18*	May 10
Methylene chloride	-	+	+
Chloroform	6	-	-
Carbon tetrachloride	20	-	13
Dichloroethane	NQ[i)]	+	9
Trichloroethylene	-	+	-
Tetrachloroethylene	NQ[i)]	+	1
Dichloropropane	-	+	+
Benzene	-	-	8
Xylene	-	+	-
Styrene	-	+	-
TOC (mg Carbon/litre)	NQ	NQ	3

All values in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)
NQ detected not quantitated
* Grab sample
i) estimated as 10 - 100 ppb

TABLE 21

Dow Chemical Canada Limited

Acid Tile - 1975 and 1977

	1975*	1977	
		April 18*	May 10
Chloroform	13	+	-
Carbon tetrachloride	110	-	+
Dichloroethane	NQ[i)]	+	+
Trichloroethylene	4	-	-
Tetrachloroethylene	NQ[i)]	+	+
Dichloropropane	NQ[i)]	-	-
Hexachlorobutadiene	-	-	NQ
Bischloroisopropyl ether	-	-	NQ
Xylene	-	-	+
Styrene	-	-	+
Diethylbenzene(s)	NQ[i)]	-	-
TOC (mg Carbon/litre)	NQ	NQ	16

All values in ug/litre (ppb)

- not detected

+ trace (0.05 - 0.1 ppb)

NQ detected not quantitated

* Grab sample

i) estimated as 10 - 100 ppb

TABLE 22

Dow Chemical Canada Limited
54" Sluice - 1975 and 1977

	1975*	1977		
		April 18*	May 10	June 21*
Methylene chloride	-	-	-	11
Chloroform	912	+	-	-
Dichlorobromomethane	150	-	-	-
Dibromochloromethane	66	-	-	-
Carbon tetrachloride	1390	-	+	5
Dichloroethane	NQ[i)]	-	+	33
Dichloroethylene	-	-	-	M
Tetrachloroethylene	NQ[i)]	+	-	6
Dichloropropane	-	-	-	M
Bischloroisopropyl ether	-	-	-	NQ
Benzene	-	+	-	-
Xylene(s)	-	+	-	-
Styrene	-	+	-	-
Diethylbenzene(s)	-	NQ	-	-
Dichlorobenzene(s)	-	-	-	NQ
Vinyl chloride	4	-	-	-
TOC (mg Carbon/litre)	NQ	NQ	18	6

All values in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)
NQ detected not quantitated
M ppm level
* Grab sample
i) estimated as 10 - 100 ppb

TABLE 23

Dow Chemical Canada Limited
Second Street Sewer - 1975 and 1977

	1975*	1977	
		April 18*	May 10
Chloroform	70	+	+
Dichlorobromomethane	21	-	-
Carbon tetrachloride	13	-	-
Dichloroethane	-	-	168
Tetrachloroethane	NQ[i)]	-	-
Tetrachloroethylene	NQ[i)]	+	-
Dichloropropane	NQ[i)]	+	-
Tetrachloropropane	NQ[i)]	+	-
Dichlorobutane	-	-	+
Hexachlorobutadiene	NQ[i)]	-	-
Bischloroisopropyl ether	-	+	+
Benzene	-	-	3
TOC (mg Carbon/litre)	NQ	NQ	20

All values in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)
NQ detected not quantitated
* Grab sample
i) estimated as 10 - 100 ppb

TABLE 24

Dow Chemical Canada Limited
Third Street Sewer - 1975 and 1977

	1975*	1977					
		April 18	May 10	May 31	June 3	June 21	July 12
Methylene chloride	-	-	-	-	-	72	13
Chloroform	-	-	5	-	-	-	-
Carbon tetrachloride	1378	+	4	-	6	+	+
Dichloroethane	-	-	33	-	-	-	-
Dichloropropane	-	+	+	-	-	-	+
4-vinylcyclohexene	-	-	-	-	-	NQ	NQ
Cyclopentadiene (or dimer)	-	NQ	-	-	-	-	
Benzene	30 ppm	+	+	13	-	940	10
Toluene	25 ppm	+	6	5	1	245	12
Xylenes	25 ppm	+	2	-	6	1400	4
Cumene	-	+	8	-	4	-	-
Styrene	200 ppm	+	-	36	-	1320	46
Methylstyrene	-	NQ	-	-	-	-	-
Trimethylbenzenes	-	-	1	7	-	3	5
Diethylbenzenes	6 ppm	-	18	12	9	-	+
Triethylbenzenes	-	-	-	NQ	1	-	NQ
Diphenyl ether	NQ[i)]	NQ	-	-	-	-	-
Naphthalene	-	+	1	1	-	64	+
Methylnaphthalene	-	-	-	11	-	195	8
Dimethylnaphthalene	-	-	-	-	-	-	NQ
Trimethylnaphthalene	-	-	-	-	-	-	NQ
Dimethyltetrahydronaphthalene	-	-	NQ	-	-	-	-
Methylindane	-	-	-	+	-	-	12
Vinyl chloride	13	-	-	-	-	-	-
TOC (mg Carbon/litre)	NQ	NQ	14	14.5	NQ	15.5	10.5

Except where stated, all values ug/litre (ppb)
* Grab sample
- not detected
+ trace (0.05 - 0.1 ppb)
NQ detected, not quantitated
i) estimated as 10 - 100 ppb

TABLE 25

Dow Chemical Canada Limited
Third Street Sewer - 1978

	May 25				May 26	
	8 am	Noon	4 pm	8 pm	8 am	Noon
Methylene chloride	1	26	4	18	118	34
Chloroform	2	3	+	1	3	1
Carbon tetrachloride	250	53	100	-	+	20
Trichloroethylene	-	7	-	+	+	-
Tetrachloroethylene	4	30	10	1	1	7
1,1-dichloroethane	3	3	8	-	-	+
1,2-dichloroethane	+*	7*	+*	1	9	6
1,2-dichloropropane	8	9	5	0.2	1	2
Butadiene	+	+	-	-	-	-
Toluene	-	-	-	-	+	-

All Grab Samples

* Estimate Peak not fully resolved from carbon tetrachloride but identified by Mass Spectrometry

All concentrations in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)

TABLE 26

Dow Chemical Canada Limited

Third Street Sewer - 1978

	October 18			October 19		
	12:00	16:00	20:50	00:00	04:10	08:00
Benzene	93	100	1920	1500	2900	610
Toluene	90	90	950	300	950	90
Ethylbenzene	260	110	940	300	1300	1420
Styrene	500	60	-	200	250	2100
C_3alkylbenzene	300	-	-	500	13	170
C_4alkylbenzene*	40	13	110	2500	40	60

Grab Samples

Note: Oil sludges and aromatics were discharged as a result of an incident in the Styrene-ethylbenzene plant at 9 p.m., October 18, 1978. Quantitation by direct aqueous injection

All concentrations in ppb (ug/litre)

* probably diethylbenzene

\- not detected

TABLE 27

Dow Chemical Canada Limited
DOEO - 1975 and 1977

	1975*	May 31, 1977
Methylene chloride	-	47
Chloroform	5	1
Carbon tetrachloride	15	-
Dichloroethane	NQ[i)]	2
Dichloropropane	-	+
Vinyl chloride	-	+
Trichloroethylene	-	+
t-Butanol	3 ppm	-
TOC (mg Carbon/litre)	NQ	5

Except as noted, all values in ug/litre (ppb)

\- not detected
\+ trace (0.05 - 0.1 ppb)
NQ detected, not quantitated
* Grab sample
i) estimated as 10 - 100 ppb

TABLE 28

Dow Chemical Canada Limited
Fourth Street Sewer - 1975 and 1977

	1975*	1977	
		April 18*	May 10
Carbon tetrachloride	100	-	-
Dichloroethane	NQ[i)]	-	+
Dichloropropane	-	+	-
Tetrachloroethylene	NQ[i)]	-	-
Bischloroisopropyl ether	-	+	+
Benzene	-	+	-
Xylene(s)	NQ[i)]	+	-
Styrene	-	+	-
Methylstyrene	-	+	-
Diethylbenzene	NQ[i)]	-	-
Dimethyldiethylbenzene	NQ[i)]	-	-
Diphenyl ether	NQ[i)]	-	-
TOC (mg Carbon/litre)	-	-	7

All values in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)
NQ detected not quantitated
* Grab sample
i) estimated as 10 - 100 ppb

TABLE 29

Dow Chemical Canada Limited

Steam Plant - 1975 and 1977

	1975*	May 10, 1977
Methylene chloride	-	3
Carbon tetrachloride	16	-
Dichloroethane	NQ[i)]	9
Tetrachloroethylene	NQ[i)]	0.3
Dichloropropane	-	+
t-butanol	3 ppm	-
TOC (mg Carbon/litre)	NQ	4

Except as noted all values in ug/litre (ppb)

- not detected

+ trace (0.05 - 0.1 ppb)

NQ detected not quantitated

i) estimated as 10 - 100 ppt

TABLE 30

Sunoco Incorporated
Total Discharge - 1975 and 1977

	1975 (Grab)	May 10, 1977
Methylene Chloride	-	+
Chloroform	-	*
Carbon tetrachloride	-	+
Dichloroethane	-	*
Tetrachloroethylene	-	*
Bischloroisopropyl ether	-	*
TOC (mg Carbon/litre)	-	7

All values in ug/litre (ppb)

- not detected

+ trace (0.05 - 0.1 ppb)

* trace; detected at similar level in intake water

TABLE 31

Shell Canada Limited
Clean (used cooling) Water - 1975 and 1977

	1975 (Grab)	May 10, 1977
Carbon tetrachloride	-	+
Tetrachloroethylene	-	+
Dichloropropane	-	*
Benzene	-	*
TOC (mg Carbon/litre)	-	3

All values in ug/litre (ppb)
- not detected
+ trace (0.05 - 0.1 ppb)
* trace; detected in intake water at similar level

Note: 1975 analyses on an in-plant sample identified, but did not quantitate, the following compounds:

dichloroethane
trichloroethylene
tetrachloroethylene
vinyl chloride

TABLE 32

Shell Canada Limited
Contaminated Water - 1975 and 1977

	1975 (Grab)	May 31, 1977
Methylene chloride	-	12
Chloroform	-	0.4
Carbon tetrachloride	12	+
Dichloroethane	-	2
Trichloroethane	-	+
Trichloroethylene	-	+
Dichloropropane	-	*
Vinyl chloride	11	-
Benzene	-	*
Toluene	-	0.1
TOC (mg Carbon/litre)	NQ	7

All values in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)

* trace: detected in intake water at similar level
NQ detected, not quantitated

TABLE 33

Ethyl Corporation of Canada Limited
Total Discharge - 1975 and 1977

	1975*	1977			
		May 10	May 31	June 21*	July 12*
Methylene chloride	-	-	-	3	3
Chloroform	NQ	-	-	-	-
Carbon tetrachloride	-	-	-	2	4
Dibromomethane	NQ	-	-	-	-
Chloroethane	-	-	M	-	-
1,2-Dichloroethane	NQ	+	M	6000	3200
Trichloroethane	NQ	-	M	-	-
1,2-Dibromoethane	-	-	M	5	38
Dichloroethylene	NQ	-	-	4	15
Dichloropropane	NQ	-	5	2	1
Trichloropropane	NQ	-	-	-	-
Trichlorobutane	-	-	1000	-	-
Dichlorobutene	-	-	30	-	-
Vinyl chloride	NQ	-	-	-	-
Vinyl bromide	NQ	-	-	-	-
Toluene	NQ	-	-	-	-
Xylenes	NQ	-	-	-	-
Naphthalene	NQ	-	-	-	-
Methylnaphthalene	NQ	-	-	-	-
TOC (mg Carbon/litre)	NQ	5	5	10	3

All values in ug/litre (ppb)
- not detected
+ trace (0.05 - 0.1 ppb)
NQ detected not quantitated
M ppm level
* Grab sample

Note: The 1975 Study identified, but did not quantitate, the following compounds in an in-plant sample:

Dichloroethane, bromochloroethane, tribromoethane, toluene, propyltoluene, naphthalene, methyl naphthalene and 6-methyl-1,2-dihydronaphthalene

TABLE 34

DuPont Canada Incorporated

Total Disharge - 1977

	May 10	May 31	July 12	August 30
Methylene chloride	7	5	10	10
Chloroform	4	+	+	+
1,2-dichloroethane	163	18	15	4
Tetrachloroethane	-	-	+	-
Tetrachloroethylene	-	1	-	1
Dichloropropane	-	0.4	0.2	0.3
Benzene	-	+	-	-
Toluene	0.3	-	-	-
TOC (mg Carbon/litre)	5	8	8	8

All concentrations in ug/litre (ppb)

- not detected

+ trace (0.05 - 0.1 ppb)

TABLE 35

Allied Chemical Canada Limited
Total Discharge - 1975 and 1977

	1975	1977		
		May 10	May 31	June 21
Chloroform	202			
Carbon tetrachloride	981	+	36	66
1,2-dichloroethane	-	+	37	-
Trichloroethane	-	NQ	-	-
Tetrachloroethylene	-	+	-	11
Dichloropropane	-	-	NQ	-
Benzene	-	+	4	-
Toluene	-	-	2	-
Xylene	-	+	0.2	-
Dichlorobenzenes	-	+	138	26
Trichlorobenzenes	-	-	80	+
Diethylbenzene	-	NQ	-	-
Naphthalene	-	-	2	-
Methylnaphthalene	-	-	-	50
Carbon disulphide	-	-	+	-
Dimethyl disulphide	-	+	-	-
TOC (mg carbon/litre)	NQ	6	6	0.5

All concentrations in ug/litre (ppb)

+ trace (0.05 - 0.1 ppb)

- not detected

NQ detected, not quantitated

TABLE 36

Beker Industries of Canada Limited
Total Discharge - 1977

	Cooling Water May 10	API Sewer May 10
Methylene chloride	3	9
1,2-dichloroethane	4	24
Dibromomethane	NQ	NQ
Dichloropropane	+	-
Xylenes	-	290
Dichlorobenzene	0.1	-
Naphthalene	0.4	-
Methylnaphthalene	16	-
TOC (mg carbon/litre)	3	9

All concentrations in ug/litre (ppb)
- not detected
+ trace (0.05 - 0.1 ppb)
NQ not quantitated

TABLE 37

Canadian Industries Limited
Total Discharge - 1975 and 1977

	1975 (Grab)	May 10, 1977
Methylene chloride	-	*
Chloroform	-	+
Benzene	-	+
Vinyl chloride	NQ	-
TOC (mg Carbon/litre)	NQ	3

\- not detected
\+ trace (0.05 - 0.1 ppb)
* trace: detected in intake water at similar level
NQ detected, not quantitated

Note: Analysis of 1975 in-plant samples identified, but did not quantitate, the following compounds:
chloroform, chloroethane, dichloropropane, vinyl chloride, formaldehyde, N-(3,4-dichlorophenyl)-N,N diethyl urea, benzene

TABLE 38

Point Edward Sewage Treatment Plant

	Final Effluent June 21, 1977
Chloroform	9
Benzene	2
Toluene	2
Xylenes	M
Trimethylbenzenes	M
Styrene	M
Cumene	M
Treatment Capacity (m^3/day)	2,590
Annual BOD_5 loading (kg)	40,800

Grab Sample

M ppm level

All other values in ug/litre (ppb)

TABLE 39

Sarnia Sewage Treatment Plant
June 21, 1977

	Raw Sewage	Final Effluent
Methylene chloride	-	+
Chloroform	-	3
1,2-dichloroethane	-	1
Trichloroethylene	+	5
Tetrachloroethylene	-	2
Dichlorobenzenes	+	1
Aliphatic hydrocarbons	+	-

Treatment Capacity (m^3/day)	65,900
Annual BOD_5 loading (kg)	550,000

Grab Samples

All values in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)

TABLE 40

Corunna Sewage Treatment Plant

	Final Effluent June 21, 1977
Methylene Chloride	5
Chloroform	2
Tetrachloroethylene	0.4
Treatment capacity (m^3/day)	1450
Annual BOD_5 loading (kg)	4300

Grab Sample

All values in ug/litre (ppb)

TABLE 41

Lambton Water Supply System
Finished Water

	May 10, 1977	June 21, 1977
Methylene chloride	95	-
Chloroform	10	14
Dichlorobromomethane	+	-
1,2-dichloroethane	-	1
Benzene	0.1	-
Toluene	1	0.2
Xylenes	5	1

8-hour composite samples

All figures in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)

TABLE 42

Lambton Water Supply System
Raw and Treated Water
1980

	February 15		February 16	
	Raw	Treated	Raw	Treated
Methylene chloride	4.7	2.0[i)]	1.1	0.5[i)]
Chloroform	0.45	4.90	0.57	7.42
Bromodichloromethane	--	9.40	0.31	10.2
Chlorodibromomethane	0.12	3.44	1.10	4.78
Bromoform	--	--	0.16	0.27
Trichloroethylene	--	0.01	--	0.01
1,1,1-Trichloroethane	--	0.02	--	--
Tetrachloroethylene	--	0.01	0.01	--
Benzene	2.22	0.90	0.65	0.65
Toluene	0.22	0.14	0.15	0.16
Ethylbenzene	--	--	0.01	--

Note: Except where noted quantitation was by MS response:
see Analytical Procedure, page 31

i) Approximate: quantitated by FID response

All values in ug/litre (ppb)

- not detected

Table 42 Cont'd

Lambton Water Supply System
Raw and Treated Water
1980

	February 17		February 18	
	Raw	Treated	Raw	Treated
Methylene Chloride	1 i)	1 i)	3 i)	1 i)
Chloroform	0.76	8.15	0.23	10.4
Bromodichloromethane	0.51	26.1	0.22	3.40
Chlorodibromomethane	0.21	6.00	0.08	3.60
Bromoform	--	0.50	--	--
Trichloroethylene	--	--	--	--
1,1,1-Trichloroethane	--	--	--	--
Tetrachloroethylene	--	--	--	--
Benzene	3.30	0.54	0.32	1.20
Toluene	0.18	0.27	0.09	0.10
Ethylbenzene	--	--	--	--

Note: Except where noted quantitation was by MS response:
see Analytical Procedure, page 31

i) Approximate: quantitated by FID response

All values in ug/litre (ppb)

- not detected

TABLE 43

River Water
Blue Water Bridge

1977

	April 18	May 31	June 21	July 12
Methylene chloride	-	4	7	5
Chloroform	-	0.1	-	-
Benzene	+	-	-	-
Toluene	+	-	+	-
Xylene(s)	+	-	+	-
Trimethylbenzenes	+	-	0.2	-
Cumene	+	-	-	-

All values in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)

TABLE 44

Imperial Oil Limited
Intake Water - 1975 and 1977

	1975	1977
Octadecanol	NQ	-
Decanol	NQ	-

- not detected
NQ detected not quantitated

TABLE 45

Polysar Limited
Intake Water - 1975, 1977 and 1978

	1975*	1977 April 18*	1977 May 10	1977 June 21	1978[i)]
Methylene chloride	-	-	10	17	-
Trichloroethylene	-	-	-	+	-
Vinyl chloride	1	-	-	-	-
Benzene	-	+	-	-	-
Xylenes	-	+	+	-	-
TOC (mg Carbon/litre)	-	-	6	5	-

All values in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)
* Grab sample

i) Composite of samples collected automatically at 1 p.m. and 6 p.m. was found to be clean. Some result was obtained with a replicate sample.

TABLE 46

Dow Chemical Canada Limited
North Intake - 1975, 1977 and 1978

	1975	1977[i]	1978[ii]
Methylene chloride	-	9	1
Chloroform	5	1	4
Dichlorobromomethane	-	-	1
Carbon tetrachloride	12	-	1
1,2-Dichloroethane	NQ[iii]	21	+
Dichloropropane	-	+	-
Tetrachloroethylene	NQ[iii]	0.3	-
t-Butanol	3 ppm	-	-
Benzene	-	-	2
Toluene	-	-	+
Xylene(s)	-	-	+
Ethylbenzene(s)	-	-	+
Diethylbenzene(s)	NQ[iii]	-	-
Dimethyldiethylbenzene(s)	NQ[iii]	-	-
TOC (mg Carbon/litre)	NQ	3	-

Except where noted, all values in ug/litre (ppb)

\- not detected

\+ trace (0.05 - 0.1 ppb)

NQ detected not quantitated

i) May 10, 1977

ii) composite of samples collected automatically at 6 p.m., Oct. 18 and 7 a.m., Oct. 19, 1978

iii) estimated as 10 - 100 ppb

TABLE 47

Dow Chemical Canada Limited
South Intake - 1975

Carbon tetrachloride	67
Dichloroethane	NQ
Tetrachloroethylene	NQ
Xylenes	NQ

Value in ug/litre (ppb)

NQ detected, not quantitated but estimated as 10 - 100 ppb.

TABLE 48

River Water
Dow Chemical Canada Limited/
Sunoco Incorporated: Fence Line

	1977			
	May 10	May 31	June 21	July 12
Chloroform	-	+	-	1
1,2-dichloroethane	+	-	-	13
Tetrachloroethane	-	-	41	-
Tetrachloroethylene	+	-	1	3
Dichloropropane	+	-	-	-
Dichlorobromomethane	-	+	-	-
Carbon tetrachloride	-	+	-	-
Trimethylbenzenes	-	-	+	-
t-butanol	-	-	+	-

All Grab Samples
All values in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)

TABLE 49

Sunoco Incorporated
Intake Water - 1975 and 1977

	1975*	May 10, 1977
Chloroform	-	+
Carbon tetrachloride	-	+
1,2-dichloroethane	-	+
Tetrachloroethylene	-	+
Bischloroisopropyl ether	-	+
TOC (mg Carbon/litre)	-	6

All values in ug/litre (ppb)
- not detected
+ trace (0.05 - 0.1 ppb)
* Grab sample

TABLE 50

River Water

Sunoco Incorporated - below dock

	May 26, 1978
Methylene chloride	1
Chloroform	1
Carbon tetrachloride (not resolved)	NQ
Tetrachloroethylene	2
1,2-dichloroethane	3*
Dichloropropane	1

Grab Sample

* Estimate, peak not resolved from carbon tetrachloride

All values in ug/litre (ppb)

NQ detected not quantitated

TABLE 51

Shell Canada Limited
Intake Water - 1975 and 1977

	1975*		May 10, 1977
Methylene chloride	-	-	+
Chloroform	-	NQ	+
Carbon tetrachloride	-	91	-
1,2-dichloroethane	-	-	+
Bromochloroethane	-	NQ	-
Tetrachloroethane	-	NQ	-
Dichloropropane	-	NQ	+
Tetrachloroethylene	-	NQ	-
5-n-butyl-4-nonene	NQ	-	-
Hydrocarbons	NQ	-	-
Benzene	-	-	+
Vinyl chloride	-	NQ	-
TOC (mg Carbon/litre)	NQ	NQ	4

All values in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)
NQ detected not quantitated
* Grab samples taken on two days

TABLE 52

River Water
Talford Creek

	May 26, 1978
Methylene chloride	5
Chloroform	9
Carbon tetrachloride*	NQ
Tetrachloroethylene	2
1,1-dichloroethane	2
1,2-dichloroethane*	NQ
Dichlorobromomethane	3
Benzene*	NQ

Grab Samples
All figures in ug/litre (ppb)

NQ detected not quantitated
* un-resolved GC peaks

TABLE 53

Allied Chemical Canada Limited
Intake Water - 1975 and 1977

	1975*	May 10, 1977
Carbon tetrachloride	19	-
1,2-dichloroethane	-	+
TOC (mg Carbon/litre)	-	4

All values in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)
* Grab sample

TABLE 54

Private Water Supplies - 1977
St. Clair Parkway

	No. 1684		No. 1785		
	May 10	July 12	May 10	June 21	July 12
Methylene chloride	15	-	4	-	-
Chloroform	1	-	1	-	-
Carbon tetrachloride	-	-	+	5	-
1,2-dichloroethane	7	20	3	5	7
Tetrachloroethylene	1	13	2	1	1
Dichloropropane	1	1	-	-	1
Dichlorobenzenes	0.3	1	-	1	0.3
Benzene	0.2	-	-	-	-
Xylenes	1	-	0.2	-	+

All values in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)
All grab samples

Note: Since 1979 No. 1684 has obtained drinking water from the Lambton Water Supply System.

TABLE 55

Beker Industries of Canada Limited
Intake Water - 1975 and 1977

	1975*	May 10, 1977
Methylene chloride	-	50
Dichlorobromomethane	-	+
1,2-dichloroethane	-	9
Tetrachloroethylene	-	1
Dichlorobenzenes	-	0.4
TOC (mg Carbon/litre)	-	3

All values in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)
* Grab sample

TABLE 56

Canadian Industries Limited
Intake Water - 1975 and 1977

	1975*	May 10, 1977
Methylene chloride	-	3
1,2-dichloroethane	-	5
Vinyl chloride	NQ	-
TOC (mg Carbon/litre)	-	3

All values in ug/litre (ppb)

- not detected

NQ detected not quantitated: estimated at trace (10 ppb) levels

* Grab sample

TABLE 57

River Water
Sombra Ferry Dock

1977

	May 31	June 21	July 12
Methylene chloride	-	8	8
Chloroform	+	-	-
Dichlorobromomethane	+	-	-
Carbon tetrachloride	-	-	8
1,2-dichloroethane	+	5	-
Trichloroethylene	-	-	1
Tetrachloroethylene	+	0.2	2

All Grab Samples
All values in ug/litre (ppb)

- not detected
+ trace (0.05 - 0.1 ppb)

TABLE 58

Fish Caught Below Imperial Oil Limited

	Benzene	Toluene	Xylenes	Trimethyl-benzene	Diethyl-benzene	Acetone	Aliphatics
Walleye	8-	-	-	-	-	NQ	-
Walleye	13	*	*	3	19	NQ	NQ
Walleye	13	15	10	5	-	-	NQ
Walleye	80	280	330	220	50	-	NQ
Walleye	*	15	15	9	*	NQ	NQ
Walleye	*	*	*	*	*	-	NQ
Walleye	*	*	*	*	*	-	NQ
Walleye	*	*	*	*	*	NQ	NQ
Walleye	49	27	21	12	7	-	NQ
Splake	110	140	60	*	*	NQ	NQ

* present but not quantitated because of hydrocarbon interferences

Concentrations ug/kg (ppb)

Detection limit 0.5 ug/kg

NQ detected, not quantitated

TABLE 59

Fish Caught Near Stag Island

	Benzene	Toluene	Xylenes	Trimethyl-benzene	Styrene	Acetone	Aliphatics
Walleye	5	18	16	+	-	-	-
Walleye	16	*	*	*	*	NQ	NQ
Walleye	11	14	+	-	-	-	NQ
Walleye	53	-	*	*	*	-	NQ
Walleye	8	12	+	*	*	NQ	NQ
Walleye	*	*	200	120	-	NQ	NQ
Walleye	7	69	15	18	15	NQ	NQ
Splake	23	21	20	-	27	NQ	NQ
Splake	22	98	17	-	-	-	-
Splake	290	130	102	51	100	NQ	NQ
Splake	12	7	-	-	15	NQ	-

* present but not quantitated because of hydrocarbon interferences

Concentrations ug/kg (ppb)

Detection limit 0.5 ug/kg

NQ detected, not quantitated

TABLE 60

Variation of Organics with Species
Fish Caught at Lambton Power
Station Outfall

	Emerald Shiner	Black Crappie	Bluegill	Pumpkin seed	Walleye
Chloroform	+	-	-	-	-
Carbon tetrachloride	-	-	-	-	+
Benzene	+	+	+	+	+
Toluene	+	+	+	+	+
Xylene	+	+	+	+	+
Styrene	+	+	+	+	+
Cumene	+	+	+	+	-
Trimethylbenzenes	+	+	+	+	-
Diethylbenzenes	+	+	+	+	+
Naphthalene	+	-	+	-	-

No quantitation was possible at the time of analysis

+ indicated compound was present

TABLE 61

Solvent Extractable Data
Sediments - 1975

Site	Solvent Extractable (mg/kg dry weight)
Sarnia Bay	526
Above Polysar	12,153
Downstream of Polysar #1 Effluent	2,854
Downstream of Polysar #2 Effluent	3,900
Downstream of Polysar #3 Effluent	1,238
Opposite flame tower of Polysar	2,559
Downstream of Polysar Final Effluent	7,185
Downstream of Dow #1 Effluent	4,264
Downstream of Dow #2 Effluent	1,035
Downstream of Dow #3 Effluent	4,264
Downstream of Dow Pumphouse	3,300
Downstream of Dow Property	240
Downstream of Shell Dock	437
Mouth of Talford Creek	1,530
Downstream of DuPont	4,010
Downstream of Petrosar Effluent	840
8th Line Drain Control	1,011
Downstream of 8th Line Drain	317
Downstream of Union Carbide Effluent	1,388
Downstream of Allied Chemical	5,206
Downstream of Chinook Chemical	2,738
Downstream of Canadian Industries	211
Downstream of Beker Industries	591
Downstream of Baby Creek	364

TABLE 62

Volatile Organics Identified in Some
St. Clair Sediments - 1975

Site	Compounds Identified
Downstream of Polysar #1 Effluent	Dichlorobenzene
Downstream of Polysar #2 Effluent	Tetrachlorobutadiene, Dimethylnaphthalene
Downstream of Dow #1 Effluent	Hexachloroethane, tetrachloroethylene, pentachlorobutadiene, hexachlorobutadiene, dichlorobenzene, trichlorobenzene
Downstream of Dow #3 Effluent	Tetrachloroethylene hexachlorobutadiene, diethylbenzene, bromochlorobenzene
Downstream of Dow Pumphouse*	Chloroform, carbon tetrachloride, hexachloroethane, trichloroethylene, tetrachloroethylene, hexachlorobutadiene
Downstream of DuPont	Alkanes
Downstream of Union Carbide	None
Downstream of Allied Chemical	None
Downstream of Chinook Chemical	Alkanes

* Approximate quantitation yielded the following values (mg/kg wet weight, ppm):

Carbon tetrachloride (200)
trichloroethylene (100)
tetrachloroethylene (400)
hexachlorobutadiene (50)

TABLE 63

PCB's in River Station Sediments

Site #*	PCB conc (ppb)	Site #	PCB conc (ppb)
1	-	37	50
2	-	38	90
3	-	39	125
5	17	40	38
6	-	41	95
7	10	42	174
8	10	43	18
10	112	44	23
11	4	46	9
12	-	47	109
13	24	48	41
14	22	50	198
18	21	51	-
19	24	52	-
20	75	53	68
21	44	54	98
22	605	55	122
23	76	56	556
24	3370	58	49
26	135	59	-
27	98	60	24
28	137	61	135
29	252	62	14
30	275	63	19
32	53	64	89
33	9	65	-
34	646	66	106
35	17	68	34
36	1080	69	46

* for location see Figure 6, page 22

TABLE 64

PCB's in Industrial Station Sediments

Site #*	PCB conc (ppb)	Site #	PCB conc (ppb)
1	-	21	348
2	24	22	395
4	-	23	130
5	-	24	270
6	-	25	320
8	19	26	68
9	-	27	104
10	285	28	-
11	-	29	27
12, 13	186	30	47
14	12	31	20
15	11	32	152
16, 17	10000	33	167
18	2280	34	72
19	368	35	72
20	80	36	38

* for location see Figure 7, page 22

TABLE 65

Wallaceburg STP

1977

	Raw Sewage			Final Effluent			
	May 31	June 12	June 21	May 31	June 12	June 21	July 12
Methylene chloride	-	-	-	3	-	-	-
Chloroform	-	-	-	15	12	10	5
1,2-dichloroethane	-	6	1	3	8	2	1
Trichloroethylene	-	-	-	-	-	-	2
Tetrachloroethylene	+	1	-	+	-	-	-
Chloroethane	+	-	-	-	-	-	-
Dichloropropane	-	+	-	-	-	-	-
Benzene	-	-	-	2	3	1	-
Dichlorobenzenes	-	0.1	-	-	+	-	4
Toluene	-	-	-	1	2	0.3	-
Xylenes	-	-	-	1	3	1	-
Trimethylbenzenes	-	-	-	+	0.3	+	-
Methylnaphthalene	+	-	-	-	-	-	-
Aliphatic hydrocarbons	-	-	+	-	-	-	+

Grab Samples

all values in ug/litre (ppb)

- not detected

+ trace (0.05 - 0.1 ppb)

TABLE 66

Little River STP. Raw Sewage and Final Effluent 1977

	Raw Sewage				Final Effluent	
	May 10	May 31	June 21	July 12	May 31	June 21
Methylene chloride	-	52	-	-	-	-
Chloroform	-	7	-	-	-	-
Carbon tetrachloride	-	3	20	-	-	-
Trichloroethylene	-	-	-	4	-	-
Tetrachloroethylene	20	-	-	-	2	1
Benzene	0.4	-	-	+	+	+
Dichlorobenzenes	1	-	+	32	2	10
Toluene	1	-	10	3	+	+
Xylenes	0.3	-	6	1	0.1	0.3
Trimethylbenzenes	5	-	18	2	-	-
Diethylbenzenes	60	-	1000	10	4	2
Naphthalene	2	-	-	-	-	-
Carbon disulphide	-	-	+	-	-	-
Dimethyl disulphide	M	M	M	-	-	-
Aliphatic hydrocarbons	+	+	-	+	-	-

All values in ug/litre (ppb)

- not detected

+ trace (0.05 - 0.10 ppb)

M at ppm level

TABLE 67

West Windsor STP. Raw Sewage and Final Effluent - 1977

	Raw Sewage	Final Effluent	
	Aug. 9	May 10	Aug 9
Methylene chloride	-	58	8
Chloroform	+	19	6
Carbon tetrachloride	-	3	20
Benzene	0.3	0.1	0.2
Dichlorobenzenes	-	-	1
Toluene	17	1	0.3
Xylenes	-	12	0.5
Trimethylbenzenes	-	0.3	+
Diethylbenzenes	0.5	-	-
Naphthalene	2	-	-
Carbon disulphide	-	-	+
Dimethyl disulphide	M	M	M
Aliphatic hydrocarbons	M	-	-

All values in ug/litre (ppb)

- not detected

+ trace (0.05 - 0.1 ppb)

M = at the ppm level

TABLE 68

Walpole Island WTP
Finished Water - 1977

	May 10	June 12
Methylene chloride	61	-
Chloroform	7	23
1,2-dichloroethane	3	11
Benzene	-	60
Toluene	-	1
Xylenes	+	50
Diethylbenzene	+	1
Trimethylbenzene	+	+

All values in ug/litre (ppb)
- not detected
+ trace (0.05 - 0.1 ppb)

TABLE 69

A. J. Brian Pumping Station (Windsor)
Raw and Finished Water - 1977

	Raw Water		Finished Water	
	June 12	June 21	June 12	June 21
Methylene chloride	-	0.5	37	-
Chloroform	-	-	19	22
Dichlorobromomethane	-	-	+	-
1,2-dichloroethane	-	0.2	-	-
Benzene	-	-	0.3	1
Toluene	-	+	0.2	0.3
Xylenes	-	+	0.2	0.4
Diethylbenzenes	-	-	6	0.2

8-hour Composite Samples
All values in ug/litre (ppb)
- not detected
+ trace (0.05 - 0.1 ppb)

TABLE 70

Fish from Lake Huron (Blue Point South) and Lake St. Clair (Puce, Mitchell's Bay and Tremblay Creek)

	Blue Point South[1]	Puce[2]			Mitchell's Bay[3]	Tremblay Creek[4]	
	#1	#1*	#2*	#3	#1	#1	#2
Chloroform	-	-	-	-	+	+	-
Tetrachloroethylene	-	-	-	-	-	-	330
Benzene	2	-	-	11	5	2	69
Toluene	1	26	7	11	3	3	26
Xylene	-	14	1	32	13	4	51
Trimethylbenzene	-	-	+	-	-	-	-
Diethylbenzene	-	-	-	-	-	-	10
Butanone	-	-	-	NQ	NQ	-	NQ
Acetone	-	NQ	NQ	NQ	-	NQ	NQ
Dimethyldisulphide	-	-	-	-	NQ	NQ	-
C_5-aldehyde	-	-	-	-	NQ	-	-
Aliphatic Hydrocarbons	NQ	-	-	+	-	-	-

Concentrations in ug/kg

Detection limits 0.5 ug/kg

* Severe foaming problems during purging

+ trace

NQ detected, not quantitated

1) White Bass

2) Walleye

3) Pike

4) #1 Walleye, #2 White Bass

TABLE 71

Tilbury North Township WTP[i)]
Finished Water
Routing Monitoring Data

Date	Chloro-form	Dichloro-bromo-methane	Dibromo chloro-methane	Carbon Tetra-chloride	Trichloro-ethylene
1978					
November 15	21	11	4	-	1
November 15*	5	3	-	-	-
December 12	8	7	4	-	-
December 12*	2	2	1	-	-
1979					
January 8	7	7	4	-	-
January 8*	3	3	-	-	-
February 5	15	10	7	-	-
February 5*	8	4	3	-	-
March 6	18	10	2	-	-
March 6*	12	5	-	-	-

All values in ug/litre (ppb)
Detection limit 0.5 ppb for chloroform
Raw water samples for each date did not contain any organics above detection limit
* Sample quenched with sodium thiosulphate
i) Water obtained from Lake St. Clair

TABLE 72

Windsor WTP. Finished Water[i)]

Routine Monitoring Results

Date	Chloro-form	Dichloro-bromo-methane	Dibromo-chloro-methane	Carbon Tetra-chloride	Trichloro ethylene
1977					
January 4 (Raw)	-	-	-	3.5	-
January 4* (Raw)	31	19	8	0.9	-
March 2	18	13	5	1.7	-
March 2*	5	3	2	2.3	-
March 2 (Raw)	-	-	-	2.1	-
March 2* (Raw)	-	-	-	2.1	-
April 4	27	12	3	-	-
April 4*	11	5	2	-	-
May 2	37	14	3	-	-
May 2*	18	6	2	-	-
June 1	42	15	4	-	-
June 1*	25	9	3	-	-
June 4	28	14	4	-	-
June 4*	19	10	4	-	-
August 2	14	7	2	-	-
August 2*	7	4	2	-	-
October 4	42	18	5	-	-
October 4*	20	9	3	-	-
1978					
February 2	20	12	4	-	8
February 2*	3	4	1	-	8

Table 72 cont'd

Date	Chloro-form	Dichloro-bromo-methane	Dibromo-chloro-methane	Carbon Tetra-chloride	Trichloro ethylene
March 1	10	8	5	0.6	-
March 1*	1	4	3	-	-
March 1 (Raw)	-	-	-	1.3	-
March 1* (Raw)	-	-	-	1.2	-
April 3	23	10	2	-	-
April 3*	9	2	-	-	-
April 3 (Raw)	-	-	-	0.3	-
April 3* (Raw)	-	-	-	0.3	-
May 1	33	14	2	-	-
May 1*	27	10	-	-	-
July 4	30	13	4	0.2	-
July 4*	16	7	2	-	-
August 1	20	9	4	-	-
August 1*	18	8	3	-	-
September 1	23	9	4	-	-
September 1*	10	5	3	-	-
October 2	13	9	4	-	-
October 2*	8	4	2	-	-
November 1	24	9	2	-	-
November 1*	8	3	1	-	-
1978					
December 1	17	8	3	-	-
December 1*	4	2	-	-	-

All values in ug/litre (ppb)
Detection limit 0.5 ppb for chloroform

Where raw water data not included, sample contained
no compounds above detection limit

* Sample quenched with sodium thiosulphate
(Raw) indicates raw water data
i) water obtained from Detroit River

TABLE 73

Amherstburg WTP. Finished Water
Routine Monitoring Data

Date	Chloro-form	Dichloro-bromo-methane	Dibromo-chloro-methane	Carbon Tetra-chloride	Trichloro-ethylene
1977					
Feburary 28	52	23	8	2.5	5
February 28 (Raw)	-	-	-	1.8	-
April 4	86	21	4	-	-
May 3	104	22	3	-	-
May 31	70	20	5	-	-
July 11	67	22	5	-	2
August 1	63	20	5	-	-
December 5	25	13	4	-	-
December 5*	10	9	5	-	-
December 5* (Raw)	-	-	-	-	-
December 12	24	12	5	-	-
December 12*	17	8	4	-	-
December 12 (Raw)	-	-	-	-	-
December 14	27	10	2	-	-
December 14*	23	10	4	-	-
December 14 (Dup)	49	16	3	-	-
1978					
January 3	50	17	3	-	-
January 3*	12	8	3	-	-
January 9	35	17	6	-	-
January 9*	16	11	4	-	-
January 23	1	14	6	-	-
January 23*	0	12	6	-	-

Table 73 cont'd

Date	Chloro-form	Dichloro-bromo-methane	Dibromo-chloro-methane	Carbon Tetra-chloride	Trichloro-ethylene
February 6	13	14	7	-	-
February 6*	5	11	6	-	-
February 13	13	14	7	-	-
February 13*	1	8	6	-	-
February 20	14	14	7	-	-
February 20*	11	13	7	-	-
February 27	6	12	9	-	-
February 27*	1	5	4	0.3	-
February 27 (Dup)	32	15	10	1.9	-
February 27* (Dup)	3	5	5	0.9	-
February 27 (Raw)	-	-	-	0.7	-
February 27* (Raw)	-	-	-	0.3	-
March 6	25	12	6	2.2	-
March 6*	3	6	4	-	-
March 6 (Raw)	-	-	-	0.9	-
March 6* (Raw)	-	-	-	1.0	-
1978					
March 13	29	14	7	1.5	-
March 13*	9	4	3	1.0	-
March 13	26	14	8	1.7	-
March 13*	12	5	4	1.0	-
March 13	23	11	8	1.1	-
March 13*	4	6	5	0.2	-
March 13 (Raw)	-	-	-	0.3	-
March 13* (Raw)	-	-	-	0.8	-
March 20	51	18	3	0.6	-
March 20*	17	3	-	0.6	-
March 20	32	13	2	0.6	-
March 20*	26	7	-	0.7	-
March 20	34	11	-	0.8	-
March 20*	34	8	-	0.8	-
March 20 (Raw)	-	-	-	0.9	-
March 20* (Raw)	-	-	-	0.8	-

Table 73 cont'd

Date	Chloro-form	Dichloro-bromo-methane	Dibromo-chloro-methane	Carbon Tetra-chloride	Trichloro-ethylene
March 28	43	12	3	-	-
March 28*	8	3	-	-	-
March 28	36	12	2	0.2	-
March 28*	14	4	-	-	-
March 28	38	12	2	0.2	-
March 28*	17	5	-	-	-
March 28 (Raw)	4	-	-	-	-
March 28* (Raw)	-			-	-
1978					
April 3	35	-	-	0.3	-
April 3*	11	-	-	-	-
April 3	38	17	4	0.3	-
April 3*	20	9	3	-	-
April 3	32	15	4	0.3	-
April 3*	23	10	3	0.2	-
April 10	40	16	4	0.2	-
April 10*	13	5	-	0.2	-
April 10	33	13	3	0.2	-
April 10*	17	8	2	-	-
April 10	23	11	2	-	-
April 10*	11	5	-	-	-
April 17	37	17	4	0.1	-
April 17*	11	6	-	-	-
April 17	31	15	4	0.1	-
April 17*	20	10	3	0.1	-
April 17	32	15	3	0.1	-
April 17*	26	15	3	0.1	-

Table 73 cont'd

Date	Chloro-form	Dichloro-bromo-methane	Dibromo-chloro-methane	Carbon Tetra-chloride	Trichloro-ethylene
April 24	64	20	-	0.2	-
April 24*	36	11	-	0.1	-
April 24	55	18	-	0.2	-
April 24*	47	14	-	0.2	-
April 24	60	19	-	0.2	-
April 24*	51	15	-	0.2	-
1978					
May 1	42	17	3	-	-
May 1*	18	8	-	-	-
May 1	40	15	-	0.1	-
May 1*	24	10	-	-	-
May 8	25	12	4	-	-
May 8*	13	7	3	-	-
May 8	29	14	5	-	-
May 8*	17	8	3	-	-
May 8	36	15	4	0.2	-
May 8*	19	9	3	-	-
May 18	24	11	5	-	-
May 18*	18	10	4	-	-
May 18	19	11	4	-	-
May 18*	16	8	4	-	-
May 18	25	12	5	-	-
May 18*	6	5	3	-	-
May 23	21	12	6	-	-
May 23*	7	6	4	-	-
May 23	21	13	6	-	-
May 23*	11	8	4	-	-
May 23	21	12	6	-	-
May 23*	17	9	4	-	-

Table 73 cont'd

Date	Chloro-form	Dichloro-bromo-methane	Dibromo-chloro-methane	Carbon Tetra-chloride	Trichloro-ethylene
1978					
May 29	24	13	5	0.3	-
May 29*	11	7	4	-	-
May 29	28	14	6	0.3	-
May 29*	14	8	4	-	-
May 29	22	12	5	-	-
May 29*	15	9	4	-	-
June 5	21	11	5	-	-
June 5*	10	6	3	-	-
June 5	24	12	5	-	-
June 5*	11	7	4	-	-
June 5	23	12	5	-	-
June 5*	11	7	3	-	-
June 12 (Raw)	20	12	6	-	-
June 12* (Raw)	11	6	4	-	-
June 12	23	10	5	-	-
June 12*	13	8	5	-	-
June 12	29	12	6	-	-
June 12*	12	7	4	-	-
June 12	169	35	4	-	2
June 12*	163	35	4	-	1
June 19	29	13	6	-	-
June 19*	8	6	4	-	-
June 19	20	10	6	-	-
June 19*	13	8	5	-	-
June 19	21	10	5	-	-
June 19*	14	8	4	-	-

Table 73 cont'd

Date	Chloro-form	Dichloro-bromo-methane	Dibromo-chloro-methane	Carbon Tetra-chloride	Trichloro-ethylene
1978					
June 26	26	12	5	-	-
June 26*	12	7	3	-	-
June 26	30	12	5	0.2	-
June 26*	21	9	4	-	-
June 26	23	10	4	-	-
June 26*	21	9	4	-	-
July 4	28	13	6	-	-
July 4*	13	8	4	-	-
July 4	28	13	6	-	-
July 4*	16	9	5	-	-
July 4	22	12	6	0.2	1
July 4*	17	9	5	-	-
July 10	31	15	5	1.3	3
July 10*	9	7	3	0.6	3
July 10	28	14	5	1.0	3
July 10*	12	7	4	0.6	3
July 10	27	14	5	0.9	3
July 10*	19	10	5	0.8	2
July 17	29	12	5	-	-
July 17*	10	6	3	-	-
July 17	28	11	5	-	-
July 17*	11	6	3	-	-
July 17	19	10	5	-	-
July 17*	16	8	4	-	-

Table 73 cont'd

Date	Chloro-form	Dichloro-bromo-methane	Dibromo-chloro-methane	Carbon Tetra-chloride	Trichloro-ethylene
1978					
July 24	23	11	5	-	-
July 24*	4	5	4	-	-
July 24	20	10	5	-	-
July 24*	15	8	4	-	-
July 24	15	8	4	-	-
July 24*	10	6	3	-	1
July 31	23	11	6	-	1
July 31*	9	6	4	-	-
July 31	18	10	6	-	-
July 31*	14	7	5	-	-
July 31	24	11	6	-	1
July 31*	13	7	5	-	1
August 8	17	11	6	-	2
August 8*	11	7	4	-	-
August 8	12	11	6	-	2
August 8*	12	7	4	-	1
August 8	15	7	5	-	1
August 8*	9	9	5	-	1
August 15 (Raw)	25	-	-	-	-
August 15* (Raw)	7	-	-	-	-
August 15	50	11	6	-	1
August 15*	47	6	5	-	-
August 21	23	11	6	-	-
August 21*	10	7	5	-	-
August 21	24	12	6	-	-
August 21*	17	9	5	-	-

Table 73 cont'd

Date	Chloro-form	Dichloro-bromo-methane	Dibromo-chloro-methane	Carbon Tetra-chloride	Trichloro-ethylene
1978					
August 28	22	8	5	-	2
August 28*	10	6	4	-	-
August 28	24	8	5	-	-
August 28*	13	6	4	-	-
September 5	17	9	5	-	4
September 5*	8	5	4	-	-
September 5	23	10	6	-	-
September 5*	13	7	5	-	-
September 11	37	16	5	-	-
September 11*	31	12	4	-	-
September 11	32	15	5	-	-
September 11*	37	11	4	-	-
September 18	7	10	6	-	-
September 18*	8	5	4	-	-
September 18	21	12	6	-	-
September 18*	15	8	5	-	-
September 25	25	11	5	-	-
September 25*	25	10	5	-	-
September 25	26	10	5	-	-
September 25*	23	10	5	-	-
October 2	24	9	5	-	-
October 2*	9	6	4	-	-
October 2	20	9	5	-	-
October 2*	10	6	4	-	-

Table 73 cont'd

Date	Chloro-form	Dichloro-bromo-methane	Dibromo-chloro-methane	Carbon Tetra-chloride	Trichloro-ethylene
1978					
October 10	20	10	5	-	-
October 10*	3	6	3	-	-
October 10	28	11	4	-	-
October 10*	13	5	3	-	-
October 16	27	11	4	-	-
October 16*	7	5	3	-	-
October 16	23	10	4	-	-
October 16*	11	6	3	-	-
October 23	30	10	4	-	-
October 23*	7	4	3	-	-
October 23	12	6	4	-	-
October 23*	8	4	3	-	-
October 30	7	5	4	-	-
October 30*	5	3	3	-	-
October 30	17	7	3	-	-
October 30*	8	5	1	-	-
November 6	26	10	4	-	-
November 6*	7	4	2	-	-
November 6	13	6	4	-	-
November 6*	10	5	3	-	1
November 14	21	9	4	-	2
November 14*	16	8	4	-	2
November 14	19	9	4	-	2
November 14*	10	6	3	-	-
1978					
November 20	26	11	4	-	2
November 20*	7	5	3	-	-
November 20	18	8	4	-	-
November 20*	8	5	3	-	-

Table 73 cont'd

Date	Chloro-form	Dichloro-bromo-methane	Dibromo-chloro-methane	Carbon Tetra-chloride	Trichloro-ethylene
November 27	24	10	4	-	2
November 27*	6	4	2	-	-
December 4	16	9	4	-	1
December 4*	5	4	2	-	1
December 4	16	10	4	-	1
December 4*	6	5	3	-	1
December 11	15	8	5	-	2
December 11*	3	3	2	-	3
December 11	17	9	5	-	2
December 11*	4	4	0	-	1
December 18	12	8	5	-	2
December 18*	3	3	2	-	-
December 18	15	9	5	-	1
December 18*	5	4	3	-	-
1979					
February 19	26	15	9	-	-
February 19*	5	5	5	-	-
February 26 (Raw)	17	10	6	-	-
February 26* (Raw)	3	3	2	-	-
1979					
February 26	3	2	2	-	-
February 26*				-	-
February 26	15	10	5	-	-
February 26*	7		3	-	-
March 5	24	-	-	0.2	-
March 5*	10	5	2	-	-
March 5	14	8	3	-	-
March 5*	10	6	3	-	-
March 19	21	10	4	0.2	-
March 19*	4	3	1	-	-

Table 73 cont'd

Date	Chloro-form	Dichloro-bromo-methane	Dibromo-chloro-methane	Carbon Tetra-chloride	Trichloro-ethylene
March 26	42	14	2	0.2	-
March 26*	14	5	-	-	-
March 26	20	8	2	0.2	-
March 26*	17	6	-	-	-
April 2	39	15	4	-	-
April 2*	6	4	2	-	-
April 2	17	10	3	-	-
April 2*	12	6	2	-	-
April 17	65	15	2	0.4	-
April 17*	20	6	-	-	-
April 17	62	15	2	0.4	-
April 17*	30	7	-	0.4	-
1979					
April 29	45	16	2	0.3	-
April 29*	47	16	2	0.3	-
April 29	48	16	3	-	-
April 29*	49	18	2	-	-
May 14	24	10	4	-	-
May 14*	11	5	3	-	-
May 14	24	10	4	-	-
May 14*	14	6	3	-	-
June 4	20	9	4	-	-
June 4*	1	3	0	-	-
June 4	8	5	2	-	-
June 4*	5	5	2	-	-
June 11	15	8	4	-	1
June 11*	3	4	2	-	-
June 11	16	8	4	-	-
June 11*	15	8	4	-	-
June 11	12	8	4	-	-
June 11*	10	7	4	-	-

Table 73 cont'd

Date	Chloro-form	Dichloro-bromo-methane	Dibromo-chloro-methane	Carbon Tetra-chloride	Trichloro-ethylene
July 9	10	5	3	-	-
July 9*	10	5	3	-	-
July 9	17	7	4	-	-
July 9*	19	7	4	-	-
July 9	13	6	4	-	-
July 9*	11	6	3	-	-
1979					
July 23	17	7	4	-	-
July 23*	16	7	4	-	-
July 23	48	13	4	-	-
July 23*	49	12	4	-	-
July 23	23	9	4	-	-
July 23*	22	9	4	-	-
August 7	25	12	6	-	-
August 7*	24	11	6	-	-
August 7	28	12	6	-	-
August 7*	26	11	6	-	-
August 7	27	12	6	-	-
August 7*	26	12	6	-	-
August 20	19	9	6	-	4
August 20*	17	11	6	-	-
August 20	17	11	6	-	-
August 20*	16	10	6	-	-
August 20	18	11	6	-	-
August 20*	17	11	6	-	-
September 4	29	14	6	-	-
September 4*	12	9	4	-	-
September 4	26	12	6	-	-
September 4*	17	10	5	-	-
September 4	24	12	6	-	-
September 4*	21	10	5	-	-

Table 73 cont'd

Date	Chloro-form	Dichloro-bromo-methane	Dibromo-chloro-methane	Carbon Tetra-chloride	Trichloro-ethylene
1979					
November 13	2	4	2	-	-
November 13*	15	9	4	-	-
November 26	16	9	5	-	-
November 26*	4	4	3	-	-
December 10	26	13	4	-	-
December 10*	9	6	3	-	-

All values in ug/litre (ppb)
Detection limit 0.5 ppb for chloroform
(Raw) indicates raw water
(Dup) indicated duplicate sample

Where raw water data not included,
sample contained no compounds
above detection limit

* Sample quenched with sodium thiosulphate

DISCUSSION

During the course of both studies, a total of eighty-four different organic compounds, excluding aliphatic hydrocarbons believed to originate from petroleum products, were identified. These have been arbitrarily divided into two classes, halogenated (mainly chlorinated) and non-halogenated, and are listed in Tables 74 and 75 respectively. A slightly higher number of compounds were observed in the extended study (57) than in the earlier one (49). Compounds identified in 1975 but not in 1977 are listed in Table 76: the table also indicates the number of times each component was observed and indicates the source (i.e. in-plant, intake or effluent). It is clear that most of the compounds were observed only once (from a total of 61 samples, 27 examined in detail) and of those observed twice, bromochloroethane was not actually detected in an industrial effluent.

A brief discussion of the possible use and origin of the compounds listed in Tables 74 and 75 is relevant.

The halogenated methanes are widespread and several are believed to originate from the disinfection of water by chlorination in STP's and WTP's (chloroform, dichlorobromomethane and dibromochloromethane). This view is supported by examination of the routine drinking water monitoring results (Tables 71, 72, 73, pages 108 ff.) where, in the vast majority of cases, the occurrence of these compounds is much higher in the finished (i.e. chlorinated) water than in the raw water. Evidence for the production of dichloromethane (methylene chloride) by aqueous chlorination is far less conclusive. The routine monitoring data implies that carbon tetrachloride is not produced in this manner but is presumably the result of industrial activity.

Many of the listed organics are widely used as industrial solvents. This includes dichloromethane, carbon tetrachloride, tri- and tetrachloroethylene, carbon disulphide and (possibly) chlorinated benzenes. Many of these are produced by industries on the St. Clair, and their presence may result from production and/or usage. Still others are intermediates or final products: 1,2 dichloroethane is manufactured as an additive for leaded gasolines where it acts as a lead scavenger; styrene, butadiene and vinyl chloride are polymer precursors; diphenyl ether, often

TABLE 74

Halogenated Organics Identified

	1975	1977
Dichloromethane (methylene chloride)	+	+
Trichloromethane (chloroform)	+	+
Tetrachloromethane (carbon tetrachloride)	+	+
Dichlorobromomethane	+	+
Dibromomethane	+	+
Tribromomethane (bromoform)	+	
Dibromochloromethane	+	
Chloroethane (ethyl chloride)	+	+
Dichloroethane (1,1 and 1,2)	+	+
Trichloroethane		+
Tetrachloroethane	+	+
Hexachloroethane	+	+
Bromochloroethane	+	
Dibromoethane		+
Dichloroethylene	+	+
Trichloroethylene	+	+
Tetrachloroethylene	+	+
Dichloropropane	+	+
Trichloropropane	+	
Tetrachloropropane		+
Chloropropene	+	
Dichloropropene	+	
Dichlorobutane		+
Trichlorobutane		+

Table 74 cont'd

	1975	1977
Dichlorobutene		+
Dichlorobutadiene	+	
Hexachlorobutadiene	+	+
Chlorocyclohexane		+
Vinyl chloride	+	+
Vinyl bromide	+	
Bis(chloroethyl)ether	+	
Bis(chloroisopropyl)ether		+
Dichlorobenzene		+
Trichlorobenzene		+
N-(3,4-dichlorophenyl)-N,N diethylurea	+	

TABLE 75

Non-halogenated Organics Identified

	1975	1977
Formaldehyde	+	
Acetone	+	
Ethanol	+	
Propanol	+	
Methyl ethyl ketone	+	
Butene		+
Buten-3-yne	+	
Butadiene		+
Di-isobutylene		+
Tri-isobutylene		+
t-Butanol	+	+
But-2-en-1-ol	+	
Butane-1,4-diol		+
Cyclohexane	+	
Cyclopentadiene		+
Diethylcyclohexane		+
4-vinyl cyclohexene		+
Decanols	+	
Octadecanol	+	
Carbon disulphide	+	+
Dimethyl disulphide		+

Table 75 cont'd

	1975	1977
Benzene	+	+
Toluene	+	+
Xylenes	+	+
Ethyl benzene	+	+
C_3alkylbenzenes: ethylmethyl, propyl, isopropyl(cumene), trimethyl		+
C_4alkylbenzenes: tetramethyl(durene), diethyl, ethyldimethyl		+
C_5alkylbenzenes: trimethylethyl	+	+
C_6alkylbenzenes: hexamethyl, triethyl, dimethyldiethyl, diisopropyl	+	+
Styrene	+	+
Methylstyrene		+
Ethylstyrene		+
Anisole		+
Diphenyl ether	+	+
Naphthalene	+	+
Methylnaphthalenes	+	+
Dimethylnaphthalenes		+
Trimethylnaphthalenes		+
6-methyl-1,2-dihydronaphthalene	+	
Dimethyltetrahydronaphthalene		+
Benzo cyclobutene or phenylacetylene	+	
Indane		+
Methylindane		+
Petroleum hydrocarbons	+	+

TABLE 76

Compounds Identified in 1975 but not in 1977

	# Observations	
Bromochloroethane	2	I,P
Tribromoethane	1	P
Trichloropropane	1	E
Chloropropene	1	E
Dichloropropene	1	E
Dichlorobutadiene	1	E
Vinyl bromide	1	E
Bis(chloroethyl)ether	1	E
N-(3,4-dichlorophenyl)-N,N diethylurea	1	P
Formaldehyde	1	P
Acetone	2	E
Ethanol	1	E
Propanol	1	E
Methylethyl ketone	1	E
Buten-3-yne	1	E
But-2-en-1-ol	1	E
Decanols	2	E
Octadecanol	1	E
6-methyl-1,2 dihydronaphthalene	1	P
Phenylacetylene	1	E

I = found in an intake water

P = found in an in-plant sample

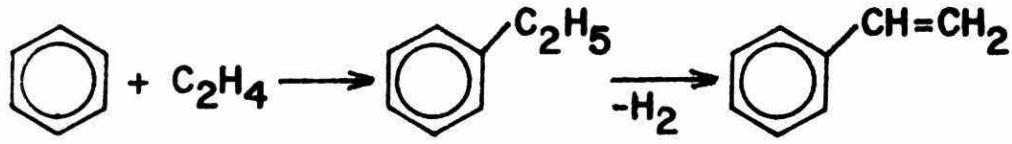
E = found in an effluent sample

formulated with diphenylmethane which was not observed, is used as a heat transfer fluid in situations where steam is inadequate. The occurrence of the latter may result from leakage from a heating system as well as from production. The higher molecular weight aromatic hydrocarbons are all suspected to be of refinery origin.

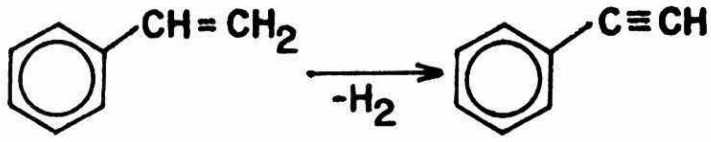
Based on a knowledge of the major industrial operations, i.e. refining, polymer production, glycol production, etc., and basic industrial chemistry, a certain amount of speculation on the origin of other listed chemicals is feasible. In the following discussion, compounds underlined have been detected in the St. Clair system.

As mentioned earlier, refinery operations can potentially release many aromatic and polycyclic aromatic hydrocarbons. Use of the purge and trap technique limits observation of the latter class to naphthalene and substituted naphthalenes, since higher molecular weight homologues do not purge well. Desulfurization processes frequently result in dimethyl disulphide and related compounds, although these are normally burnt. Iso-butylene may be dimerized to diiso-butylene (iso-octene) and hydrogenated to produce iso-octane for use as a gasoline additive. Triisobutylene can be a by-product of the dimerization process.

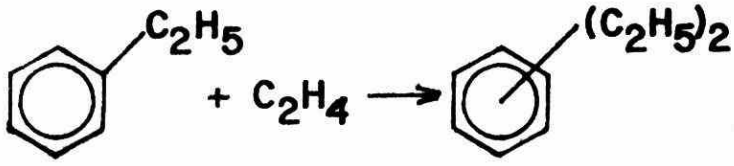
Polymer production often starts with styrene and butadiene monomers. Styrene is produced by dehydrogenating ethylbenzene that is, in turn, produced by reacting ethylene and benzene:

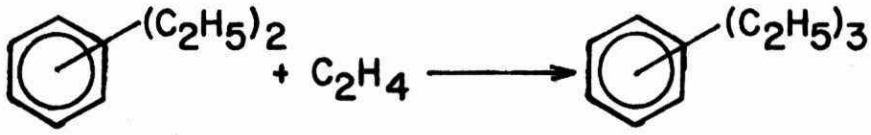


Further dehydrogenation of styrene can produce phenylacetylene:

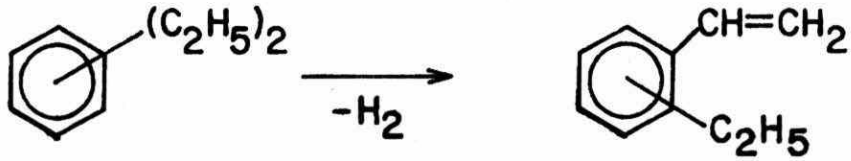


Further reaction of ethylbenzene and ethylene produces diethyl and triethyl benzenes:



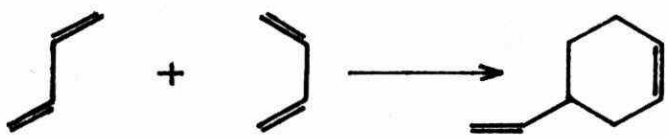


and dehydrogenation of these would result in a variety of by-products, for example ethylstyrene:



Naturally, the situation is further complicated by feedstock impurities. Thus propene impurities in the ethylene could lead to propyl, dipropyl and tripropyl-benzenes; toluene and xylene impurities in the benzene would produce methyl-styrene, dimethylstyrene, etc. Alpha-methylstyrene is a by-product of phenol manufacture and is often used in co-polymers.

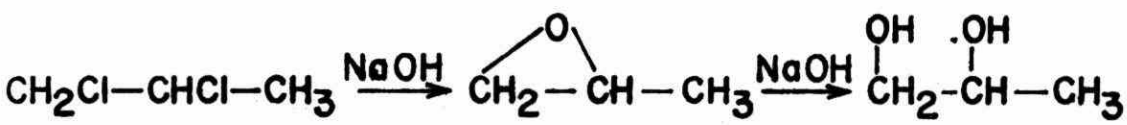
Butadiene can be produced by a variety of methods including the dehydro-genation of butene. Butadiene itself can dimerize to form 4-vinyl cyclohexene:



Classical methods for the production of polyglycols often involve the formation of chlorinated intermediates, for example polypropylene glycols may be produced as follows. Propene is reacted with chlorine to produce dichloropropane:

$$CH_2{=}CH{-}CH_3 + Cl_2 \longrightarrow CH_2Cl{-}CHCl{-}CH_3$$

which is treated with sodium hydroxide to produce an epoxide that can react further with water to form propylene glycol:



An alternative route involves production of chlorohydrin from propene, chlorine and water:

$$CH_2{=}CH{-}CH_3 \xrightarrow{Cl_2, H_2O} CH_2Cl{-}CHOH{-}CH_3$$

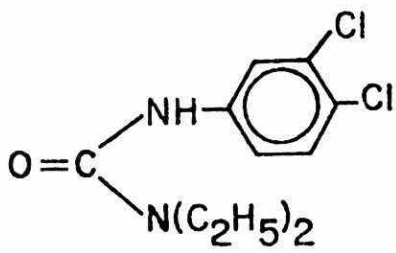
which leads to the same epoxide. In both of these methods bis(chloroisopropyl) ether can be produced as a by-product.

A competing reaction between chlorine and propene produces chloropropene:

$$CH_2{=}CH{-}CH_3 \xrightarrow{Cl_2} \begin{matrix} CHCl{-}CH{-}CH_3 \\ \underline{or} \\ CH_2{-}CHCl{-}CH_3 \end{matrix}$$

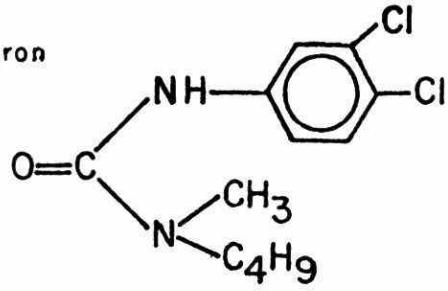
Polyglycols based on ethylene and butene can be produced in a similar fashion suggesting that dichloroethane, chloroethylene, dichlorobutene, chlorobutene, bis-(chloroethyl)ether, etc. may arise from similar processes. Side reactions might also produce dichloroethylene, dichloropropene and dichlorobutene. Again the situation can be complicated by feedstock impurities, and the chlorinated ethanes and butadienes are thought to occur from this source.

In short, the occurrence of all the compounds listed in Tables 74 and 75 can be quite easily explained in terms of known processes and products, raw materials and simple chemistry. Only two compounds are thought unlikely. Benzocyclobutene is generally unstable but the mass spectral data could not distinguish between this compound and phenylacetylene; it is thought that the compound observed was, in fact, phenylacetylene, the presence of which can be explained. The other curiosity is N-(3,4 dichlorophenyl)-N,N-diethylurea, which was observed in an in-plant sample collected at the Canadian Industries Limited plant in 1975. The structure of this compound:

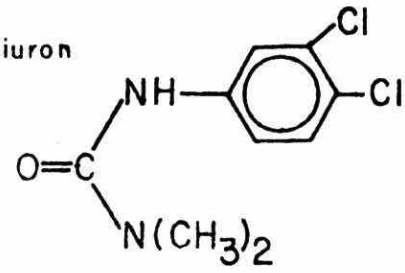


suggests that it is related to the herbicides Neburon and Diuron:

Neburon



Diuron



and hence, its occurrence may not be unreasonable. It seems, however, highly unlikely that a compound of this type would purge well.

Any discussion of the significance of the occurrence of a particular compound must necessarily be incomplete since many factors, from the viewpoint of impact on human and environmental health, affect the situation. Some of the relevant parameters are:

i) quantity and frequency of occurrence

ii) toxicity, mutagenicity, etc.

iii) bio-accumulation potentials

iv) synergistic and antagonistic effects

v) dispersion and loss effects (mixing, degradation, volatilization, sedimentation, etc.)

The majority of these points are concerned with the transportation of organic compounds from source to receiving organism and with the effects on that organism thereafter.

In an attempt to control pollution, however, the fundamental concern is source identification which, in the case of an heavily industrialized area such as the St. Clair, may be difficult. Although an enormous amount of data has been presented in the preceding section, no site, with the exception of Dow Third Street Sewer and Polysar Stereo API sampled in 1978, was examined more than six times. This is

inevitable in a study with a wide scope, but renders positive identification of source statistically uncertain. Nevertheless, the nature of the analytical methodology is such that confidence in a particular compound being associated with a particular site is good. This is especially true if the concentration is high since artifacts (contamination, etc.) are then less likely. In consequence,it is felt that the major purpose of this Report is to highlight areas of potential concern that necessitate additional abatement action or require additional in-depth study, which was one of the goals of the investigation study (see Foreword). Clearly, any areas of concern identified will be effluents, either industrial or from a STP and, while such areas can be identified from the organic data only, a more complete picture is obtained by considering the other Reports in the St. Clair Study Series.

In considering the significance of a particular site, a variety of criteria could be applied, for example:

i) How many organic compounds were observed?

ii) What are the concentrations: are any in excess, for example, of 1 ppm?

iii) What is the frequency of occurrence?

iv) What is the TOC value and the corresponding organic loading?

v) Are any of the compounds known to present a bio-hazard?

With reference to the impact on the environment or human health, point v) is clearly the most important. Unfortunately, knowledge of health significance of hazardous materials lags far behind the ability to analyze for them, but the other points compensate for this since large quantities of organics are environmentally undesirable. Data on the bio-hazards presented by various compounds has been obtained from the Toxicity Data for ten of the more common compounds (Appendix 1), the Mutagenicity Testing Report in this series, and from the Ontario Government "Blue Book" ("Water Management - Goals, Objectives and Implementation Procedures of the Ministry of the Environment". Ministry of the Environment, November 1978).

The Mutagenicity Report ("St. Clair River Organics Study. The Detection of Mutagenic Activity; Screening of Twenty-three Compounds of Industrial Origin", Ministry of the Environment, November 1979) presents the results of a mutagenic screening of twenty-three compounds identified in the 1975 organic study. The report indicates that five compounds were found to be mutagenic although a literature survey indicated slightly different results. The mutagenic and carcinogenic compounds are summarized in Table 77. Throughout the following discussion, particular attention is paid to the occurrence of these compounds.

Tables 78 and 79 indicate the frequency of occurrence of the halogenated and non-halogenated compounds respectively, in the effluents. The data is presented for 1975 and 1977 taken together (1978 is ignored because it was restricted to high frequency sampling at a limited number of sites) in two ways - by site and by sample. For the former, by site, a compound is counted if it was observed on at least one occasion at a particular site; the number of samplings is ignored. The frequency by sample indicates the total number of times a compound was observed. These tables show several interesting features. Firstly, few compounds are widespread; only methylene chloride, chloroform, carbon tetrachloride, dichloroethane, trichloroethylene, tetrachloroethylene, dichloropropene, vinyl chloride, benzene, toluene, xylene and the naphthalenes occur regularly. The vinyl chloride observations mainly refer to 1975, when a specific vinyl chloride assay was included in the study. The occurrence of these compounds in particular arises from their widespread use as solvents and raw materials. Secondly, certain compounds observed and listed in Tables 74 and 75 are not given frequency of occurrence figures. This indicates that these compounds were not detected in effluents but appeared in intake waters or (1975 study) in in-plant samples. This is particularly important for one compound shown in the Mutagenicity study to be mutagenic: bromochloroethane. This compound was detected only in 1975: once in an in-plant sample (Ethyl Corportation of Canada Limited) and once in an intake water (Shell Canada Limited). Trichoropropane, another compound shown to be mutagenic in this study, was again only observed in 1975 and only on one occasion. The occurrence of these compounds is not, therefore, regarded as especially significant: they are, however, both associated with the Ethyl Corporation which, for other reasons, is recommended for further study and the possibility of occurrence of these compounds should be examined.

TABLE 77

Summary of Mutagenic and Carcinogenic Compounds Identified by the Mutagenicity Report[i)]

	Mutagenic in Reported Study	Literature Survey Results	
		Mutagenic	Carcinogenic
Dichloromethane	+	+	+
Chloroform	-	-	+
Carbon tetrachloride	-	-	+
Bromoform	-	+	+
1,1-Dichloroethane	+		
1,2-Dichloroethane	+	+	+
1,2-Bromochloroethane	+	+	
1,1,2,2-Tetrachloroethane	-	+	
1,1,2-Trichloroethylene	-	(+)	+
1,2,3-Trichloropropane	+		
Benzene	-	-	+

- not active

+ active

(+) activity less than 2.5

i) St. Clair River Organics Study.
The Detection of Mutagenic Activity;
Screening of Twenty-three Compounds of Industrial Origin.
Ministry of the Environment, November 1979.
Table 5, page 15.

TABLE 78

Frequency of Occurrence of
Halogenated Organics in Effluents
1975 and 1977

	Code	By Site (out of 31)	By Sample (out of 88)
Dichloromethane (methylene chloride)	P,C,M	20	30
Trichloromethane (chloroform)	C	22	33
Tetrachloromethane (carbon tetrachloride)	C	16	31
Dichlorobromomethane		2	2
Dibromomethane		2	3
Tribromomethane (bromoform)	M,C	-	-
Dibromochloromethane		1	1
Chloroethane (ethyl chloride)		2	2
Dichloroethane (1,1 and 1,2)	P(1,1 and 1,2),C,M(1,2)	18	38
Trichloroethane		5	6
Tetrachloroethane	M	4	6
Hexachloroethane		2	2
Bromochloroethane	P	-	-
Dibromoethane		1	3
Dichloroethylene		3	5
Trichloroethylene	C,M	8	11
Tetrachloroethylene		14	26
Dichloropropane		15	26
Trichloropropane	P	1	1
Tetrachloropropane		1	2
Chloropropene		1	1
Dichloropropene		-	-

Table 78 cont'd

	Code	By Site (out of 31)	By Sample (out of 88)
Dichlorobutane		1	1
Trichlorobutane		1	1
Dichlorobutene		1	1
Dichlorobutadiene		-	-
Hexachlorobutadiene		5	5
Chlorocyclohexane		-	-
Vinyl chloride		13	13
Vinyl bromide		1	1
Bis(chloroethyl)ether		-	-
Bis(chloroisopropyl)ether		5	7
Dichlorobenzene		3	5
Trichlorobenzene		1	2

P - showed mutagenic activity in present study

M - known mutagen

C - known carcinogen

- not detected in effluent

TABLE 79

Frequency of Occurrence of
Non-halogenated Organics in Effluents
1975 and 1977

	Code	By Site (out of 31)	By Sample (out of 88)
Formaldehyde		-	-
Acetone		2	2
Ethanol		1	1
Propanol		2	2
Methyl ethyl ketone		1	1
Buten-3-yne		1	1
Butene		-	-
Butadiene		3	4
Di-isobutylene		-	-
Tri-isobutylene		-	-
t-Butanol		4	5
But-2-en-1-ol		1	1
Butane-1,4-diol		1	1
Cyclopentadiene		1	1
Cyclohexane		1	1
Diethylcyclohexane		-	-
4-vinyl cyclohexene		1	2
Decanols		-	-
Octadecanol		-	-
Carbon disulphide		2	2
Dimethyl disulphide		1	1

Table 79 cont'd

	Code	By Site (out of 31)	By Sample (out of 88)
Benzene	C	18	29
Toluene		13	23
Xylenes		16	29
Ethyl benzene		-	-
C_3alkylbenzenes: ethylmethyl, propyl, isopropyl(cumene), trimethyl		5	12
C_4alkylbenzenes: tetramethyl(durene), diethyl, ethyldimethyl		8	13
C_5alkylbenzenes: trimethylethyl		-	-
C_6alkylbenzenes: hexamethyl, triethyl, dimethyldiethyl, di-isopropyl		2	2
Styrene		8	14
Methylstyrene		4	4
Ethylstyrene		-	-
Anisole		-	-
Diphenyl ether		2	3
Naphthalene		7	15
Methylnaphthalenes		7	12
Dimethylnaphthalenes		2	2
Trimethylnaphthalenes		1	1
6-methyl-1,2-dihydronaphthalene		-	-
Dimethyltetrahydronaphthalene		1	1
Benzo cyclobutene or phenylacetylene		-	-
Indane		1	1
Methylindane		2	4
Petroleum hydrocarbons		1	3

C - known carcinogen

Presenting frequency data as in Tables 78 and 79 has several problems. In particular it gives no guide to distribution but merely indicates how widespread the distribution is and, second, gives no indication of concentration. Concentration data is available in the analytical results section and will be discussed presently. The distribution of organics is ilustrated in Figures 9 and 10, which present the frequency of occurrence of the twelve compounds most widespread by sample. Each site is associated with a number, for ease of presentation, which are listed in Table 80. The figures show plots for each compound separately on axis with an abscissa scale of zero to one. The value is calculated by representing each observation by sample, at a particular site, as a fraction, i.e. two observations out of four samples yields a value of 0.5. Thus the figures indicate the likelihood of a particular compound being present at a given site, except where the number of analyses (also listed in Table 80) was one which is statistically unreliable. This data is calculated for 1975, 1977 and 1978 since it is expressed as a fraction and the higher frequency 1978 sampling only helps to improve the reliability where appropriate. It must be stressed that the figures do not indicate concentrations but rather the frequency of occurrence at a particular site. Thus where a value of one is indicated for a site, the compound was observed in all samples analyzed from that site. Where the number of samples is one (sites 1, 5, 6, 27, 29 and 30) little meaning can be attached to the frequency of occurrence. Vinyl chloride data is undoubtedly somewhat unrealistic as a current picture since a specific assay was used in 1975 but not in other years.

In spite of these weaknesses, the Figures do show some interesting features. Methylene chloride and chloroform are clearly, and not surprisingly, widespread since they were found at the majority of sites and there is no obvious pattern to their occurrence. Carbon tetrachloride, 1,2-dichloroethane, tri- and tetrachloroethylene and dichloropropane on the other hand show a quite distinctive pattern. With the exception of site 3, for trichloroethylene, and site 6, for dichloroethane, trichloroethylene and tetrachloroethylene, these compounds are observed sporadically upstream of Dow (sites 12 to 21): thereafter, they were observed regularly. Since site 6 is one of those only analyzed once, the peak at this point is of somewhat dubious significance. Below Dow, carbon tetrachloride showed a regular appearance at sites 24 (Shell Contaminated Water) and 28 (Allied Chemical). Dichloroethane appeared regularly at sites 25 (Ethyl Corporation), 26 (DuPont Canada), 29 and 30 (Beker Industries - one analysis). In view of the extremely high

Figure 9. Frequency of Occurrence of Selected Organics vs. Site (from Table 80).

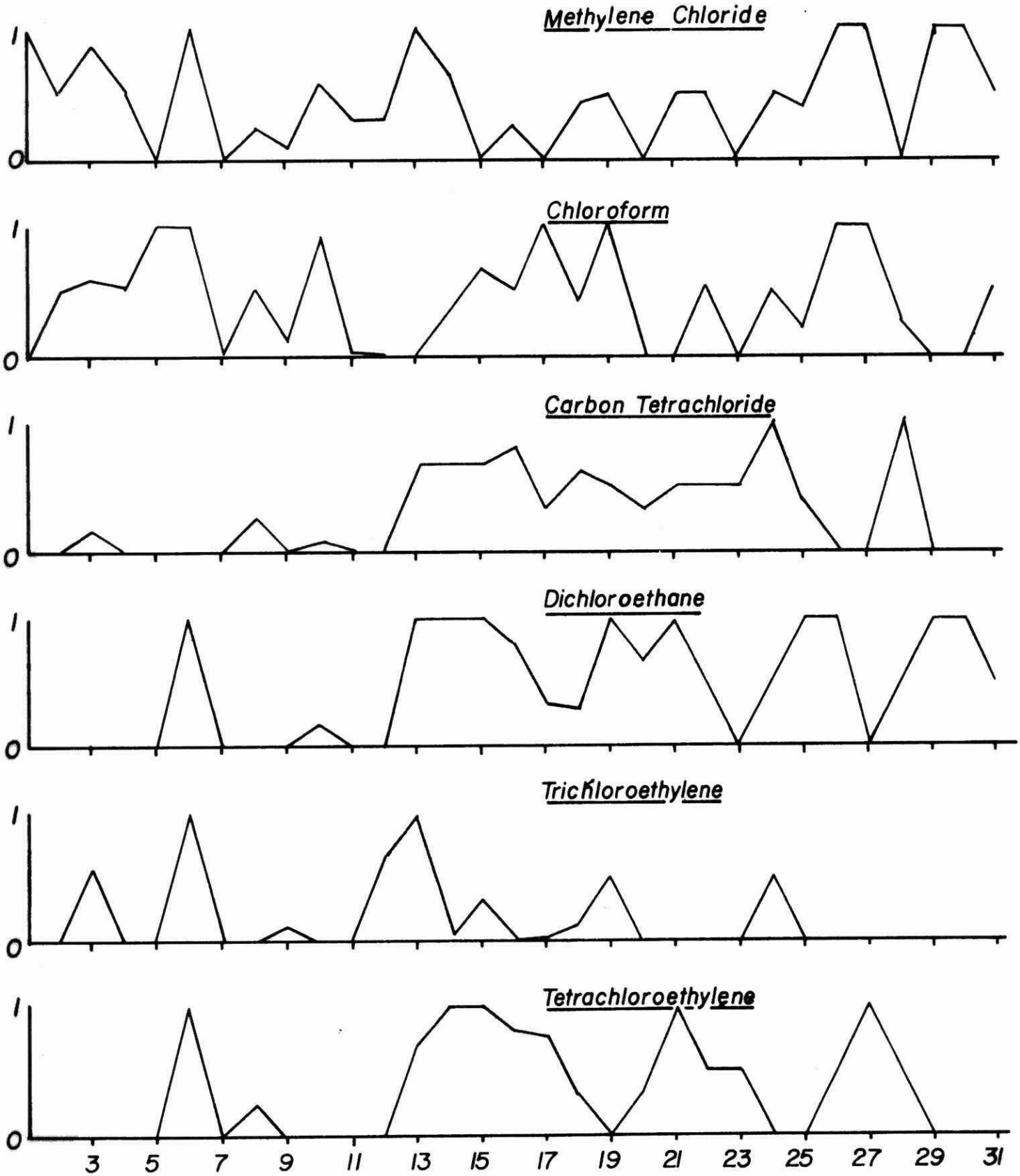


Figure 10. Frequency of Occurrence of Selected Organics vs. Site (from Table 80.)

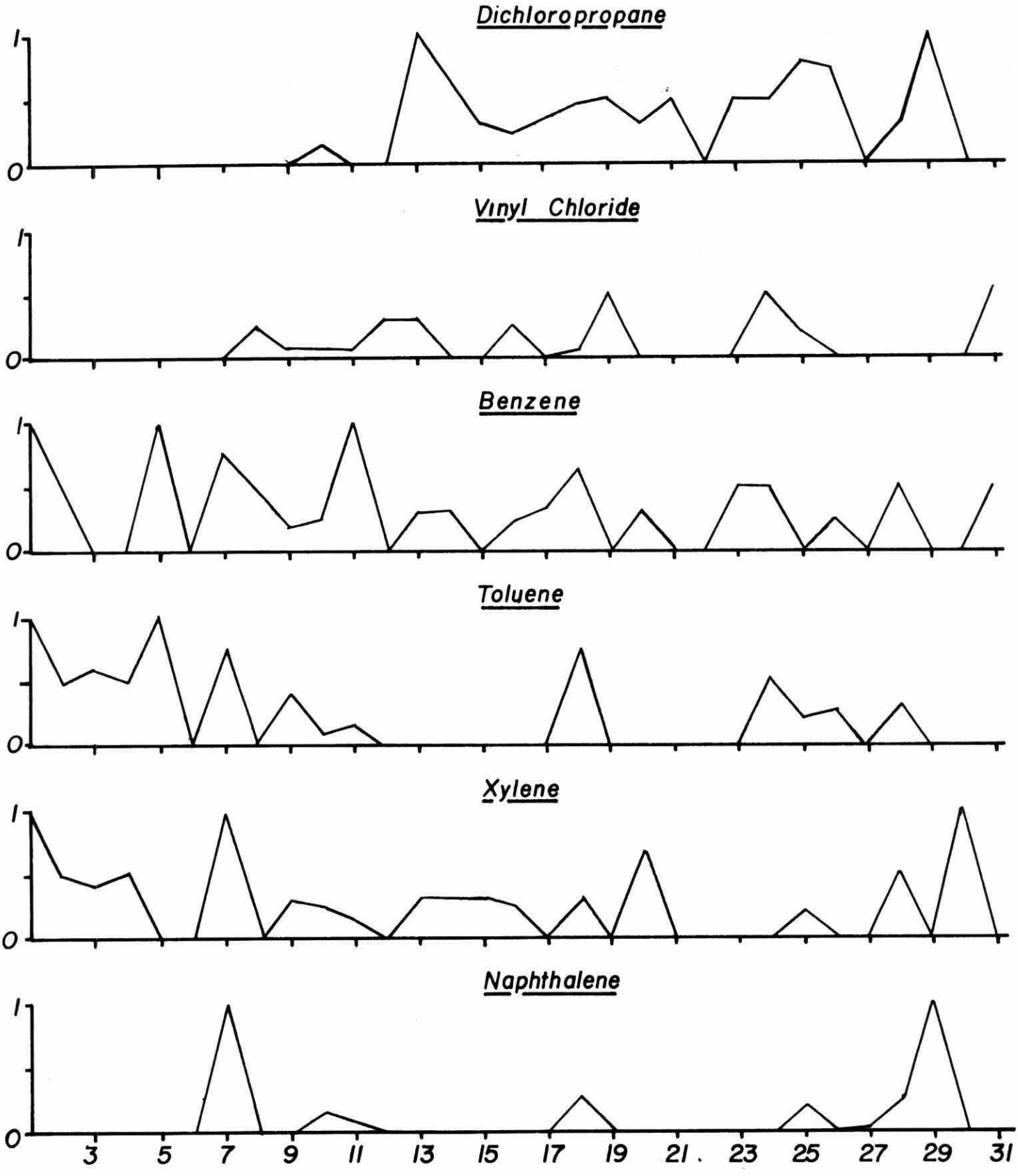


TABLE 80

Code Numbers of Sites for
Figures 9 and 10

Site	Code	# Analyses
Pt. Edward STP Final Effluent	1	1
Imperial Oil Limited		
#3 Separator	2	2
#9 Separator	3	2
#11,#12 Separator	4	2
Bio-oxidation Unit	5	1
Sarnia STP Final Effluent	6	1
Esso Chemical Canada Limited - Pressure Sewer	7	4
Polysar Limited		
Township Ditch	8	4
54" Sewer	9	4
66" Sewer	10	4
Stereo API	11	4
72" Sewer	12	3
Dow Chemical Canada Limited		
42" Sewer	13	3
48" Sewer	14	3
Acid Tile	15	3
54" Sluice	16	4
Second Street Sewer	17	3
Third Street Sewer	18	7
D.O.E.O.	19	2
Fourth Street Sewer	20	3
Steam Plant	21	2
Sunoco Incorporated		
- Total Discharge	22	2

Table 80 cont'd

Site	Code	# Analyses
Shell Canada Limited		
Clear Water	23	2
Contaminated Water	24	2
Ethyl Corporation of Canada Limited - Total Discharge	25	5
DuPont Canada Limited - Total Discharge	26	4
Corunna STP. Final Effluent	27	1
Allied Chemical Canada Limited	28	4
Beker Industries of Canada Limited		
Cooling Water	29	1
Stereo API	30	1
Canadian Industries Limited - Total Discharge	31	2

concentrations of this compound found at Ethyl (see Table 33, page 69) the occurrence downstream may well have resulted from carry-over. The pattern for trichloroethylene shows sporadic appearances up to site 24 (Shell Contaminated Water). The graph for tetrachloroethylene suggests that this compound is concerned mainly with the Dow operation: major occurrences at site 6 and 27 are of less significance due to single analysis for these sites; however, frequent occurrences at sites 22 (Sunoco), 23 (Shell Clean Water) may arise from carry-over. Dichloropropane, again, occurs in almost every site below Dow: a major occurrence at site 29 (Beker Cooling Water) again corresponds to a single sampling. The aromatic hydrocarbon graphs shows no clear pattern: benzene appears widespread but mainly associated with Imperial Oil Bio-oxidation Unit (site 5), Esso Chemical (site 7) and Polysar Stereo API (site 11); toluene was observed regularly at Imperial Oil Bio-oxidaton Unit (site 5), Esso (site 7) and Dow Third Street Sewer (site 18); xylenes were observed regularly at Esso (site 7), Dow Fourth Street (site 20), Allied Chemical (site 28) and Beker Stereo API (site 30 - single analysis); naphthalene is mainly related to Esso (site 7) and Beker Cooling Water Discharge (site 29 - single analysis): the latter may arise from carry-over.

In short, these Figures serve to pinpoint certain sites, Imperial Oil, Esso Chemical, Polysar Incorporated, Dow Chemical, Allied Chemical and Beker Industries, which bear a more detailed analysis of the available data. As mentioned previously, there are a variety of other criteria that can be applied in deciding areas for a more thorough analysis. Figure 11 contains graphs of mean organic loading, TOC and the number of organic compounds observed plotted against site number, as in Table 80. This data is for 1977 only. A line at 5 mg Carbon/litre on the TOC curve indicated the "Blue Book" guideline for drinking water quality and it is clear that many sites are close to this value. Blank spots correspond to STP's that were not sampled for TOC. Obvious maxima occur as follows: sites 9 and 10 (Polysar 54" Sewer and 66" Sewer), 18 (Dow Third Street Sewer) and 20 (Dow Fourth Street) for mean organic loading. Sites 5 (Imperial Oil Bio-oxidation Unit), 7 (Esso Chemical), 9 and 11 (Polysar 54" Sewer and Stereo API Sewer) for TOC. Sites 7 (Esso Chemical), 16 (Dow 54" Sluice), 18 (Dow Third Street Sewer) and 28 (Allied Chemical) for number of organics observed.

From the preceding discussion, it appears therefore that the following sites need a closer examination of the relevant data:

Site #	Site	Reasons
5	Imperial Oil Bio-oxidation Unit	Benzene, toluene
7	Esso Chemical Pressure Sewer	Benzene, toluene, xylene, naphthalene, TOC
9	Polysar 54" Sewer	Organic loading
10	Polysar 66" Sewer	Organic loading, TOC
11	Polysar Stereo API	Organic loading, TOC
16	Dow 54" Sluice	Number of organics
18	Dow Third Street Sewer	Toluene, organic loading, number of organics
20	Dow Fourth Street Sewer	Xylene, organic loading
12-21	All Dow Sites	Chlorinated compounds
22	Sunoco Incorporated Total Discharge	Tetrachloroethylene (carry-over?)
23	Shell Canada Clean (Used Cooling) Water	Tetrachloroethylene (carry-over?)
24	Shell Contaminated Water	Carbon tetrachloride, trichloroethylene
25	Ethyl Corporation Total Discharge	Dichloroethane
26	Dupont Canada Total Discharge	Dichloroethane
28	Allied Chemical Canada Total Discharge	Carbon tetrachloride, xylene, number of organics
29	Beker Industries of Canada Used Cooling Water	Dichloroethane, (dichloro-propane, naphthalene (all carry-over?)
30	Beker Industries of Canada Stereo API	Dichloroethane, xylene (carry-over?)

In attempting to decide whether carry-over of organics is occurring, it is instructive to examine the intake water data. The reason for this is that in some of the cases listed above, significant organics are found in used cooling water discharges (i.e. sites 23 and 29) that are downstream of sites apparently discharging the same organics. Table 81 lists the organic compounds, and frequency of occurrence, of organics found in Samples Indicating River Water Quality, i.e. industrial, municipal and private intakes in addition to river water samples. This data summarizes all sampling occasions (1975, 1977 and 1978) in order to maximize the database. It is clear that fewer compounds were observed in the intakes than in the effluents (cf. Tables 78, 79 and 81) but that similar compounds are most prevalent, i.e. methylene chloride, chloroform, carbon tetrachloride, 1,2-dichloroethane, tetrachloroethylene and benzene. Naphthalene was not observed in any intake implying that it is easily lost, perhaps by sedimentation (it is insoluble in water), bio-degradation or bio-accumulation. Comparing the incidence by site (i.e. number of sites compound observed at divided by number of sites) the following figures are obtained:

	Effluents	Water Quality Samples
Methylene Chloride	0.65	0.69
Chloroform	0.71	0.56
Carbon tetrachloride	0.52	0.63
1,2-Dichloroethane	0.58	0.81
Trichloroethylene	0.25	0.13
Tetrachloroethylene	0.45	0.63
Dichloropropane	0.48	0.31
Vinyl Chloride	0.42	0.19
Benzene	0.58	0.44
Toluene	0.42	0.19
Xylene	0.52	0.38
Naphthalene	0.23	0

These values show some small differences, viz. dichloroethane and tetrachloroethylene more widespread in Water Quality Samples than in effluents, but otherwise are quite similar.

Figure II. Loading, TOC and No. of Organics vs. Site
(from Table 80)

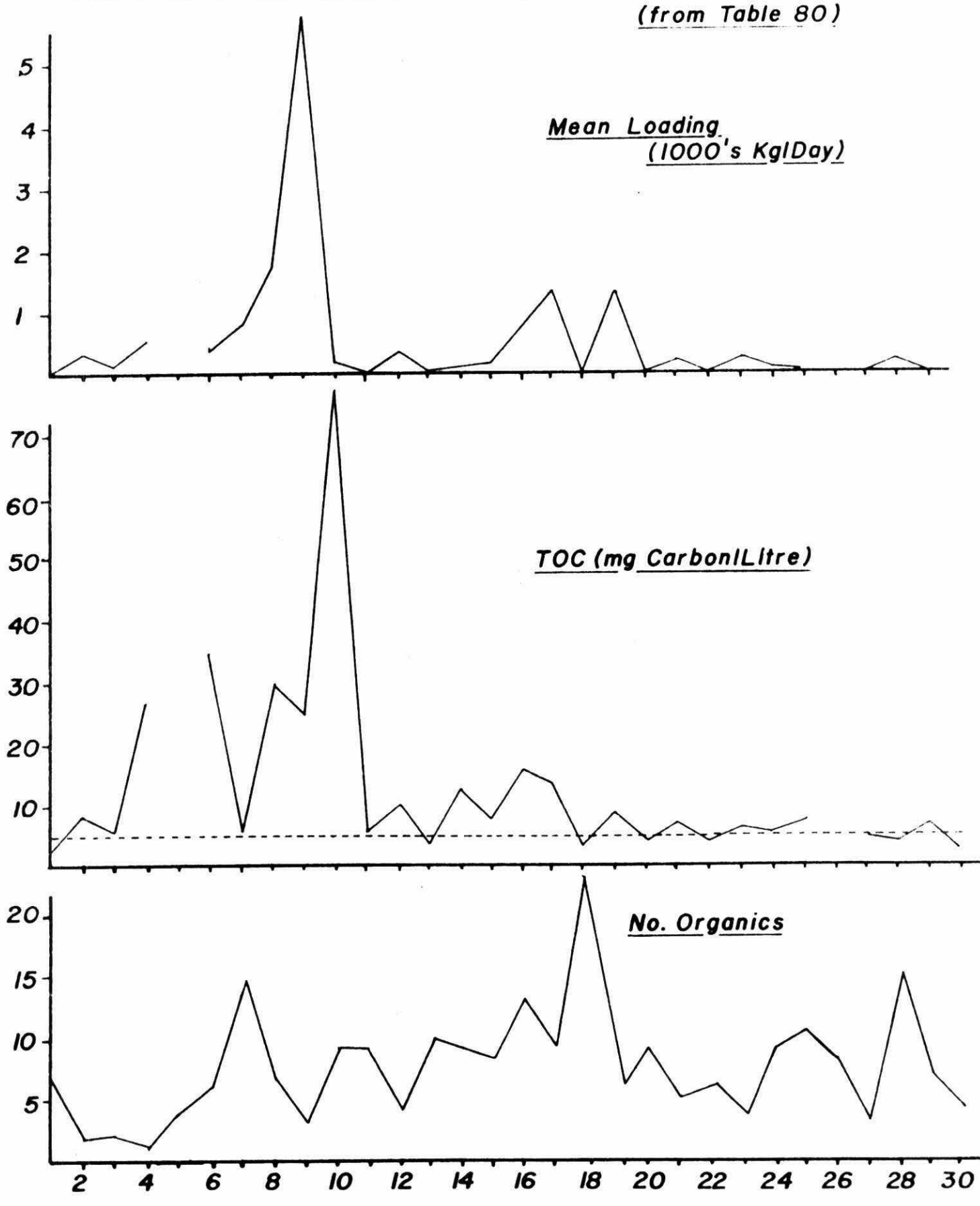


TABLE 81

Overall Frequency of Occurrence of Organics in River Water Quality Samples

	Code	By Site[i] (out of 16)	By Sample (out of 42)
Vinyl chloride	M	3	3
Methylene chloride	P,C,M	11	17
Chloroform	C	9	16
Dichlorobromomethane		6	6
Carbon tetrachloride	C	10	12
1,1-Dichloroethane	P,M	1	1
1,2-Dichloroethane	P,C,M	13	21
Bromochloroethane	P,M	1	1
Tetrachloroethane	M	2	2
Dichloropropane		5	8
Trichloroethylene	M,C	2	2
Tetrachloroethylene		10	19
Bis(chloroisopropyl)ether		1	1
Dichlorobenzene		2	5
Benzene	C	7	7
Toluene		3	5
Xylene		6	11
Ethylbenzene		1	1
Trimethylbenzene		2	2
Diethylbenzene		1	1
Cumene		1	1
Dimethyldiethylbenzene		1	1
t-Butanol		2	2
Decanol		1	1
Octadecanol		1	1
5-n-butyl-4-nonene		1	1
Hydrocarbons		1	1

i) detected on at least one occasion at a particular site
P mutagenic activity detected in present study
C known carcinogen
M known mutagen (see Biohazards Report)

The distribution of the six most widespread compounds in Water Quality samples is illustrated in Figure 12 for the site numbers, and number of analyses, listed in Table 82. Values for site 1, Lambton Water Supply System, are probably not representative since these samples are of finished water. Nevertheless, the distributions are remarkably similar. Methylene chloride and chloroform are widespread in the entire system whereas the other chlorinated compounds do not become prominent until Dow Chemical, site 5. The occurrence of benzene appears to be linked to the refineries operations at Imperial Oil and Shell Canada since it is observed below these sites. Considering the cases where carry-over is suspected (from page 144) at effluent site 22 (Sunoco Incorporated Total Discharge) tetrachloroethylene was also found in the intake, similarly for site 23 (Shell Canada Used Cooling Water). Dichloroethane was found in the intake to Beker Industries.

As yet no reference has been made to the concentration factor: in the site-by-site discussion that follows, additional significance is attached to compounds that are observed regularly in excess of 100 ppb and sporadically in excess of 1 ppm. While these figures are purely arbitrary, and may appear high, they are thought reasonable since dilution effects will reduce the impact except in the immediate vicinity of each outfall.

i) Industrial Effluents

Imperial Oil

The Imperial Oil operation on the St. Clair River involves typical refinery processes to prduce a range of petroleum products. Wastes are discharged through three sewers, which carry the water from oil/water separators (#3, #9 and #11,12 Separators); one also discharges treated waste from a Bio-oxidation unit. Earlier in this section the Bio-oxidation effluent was identified as a potential area of concern on the basis of a high mean TOC (26.7 mg Carbon/liter) value and aromatic hydrocarbon discharges; this is borne out by the analytical results. The separator effluents had low mean TOC values (3 - 8.3 mg Carbon/liter, Table 1, page 15) and organics were occasionally observed at low ppb levels (see Tables 4 to 7). The only significant occurrence was methylene chloride observed in all samples (5) collected

Figure 12. Frequency of Occurrence of Selected Organics vs. Water Quality Site (from Table 82).

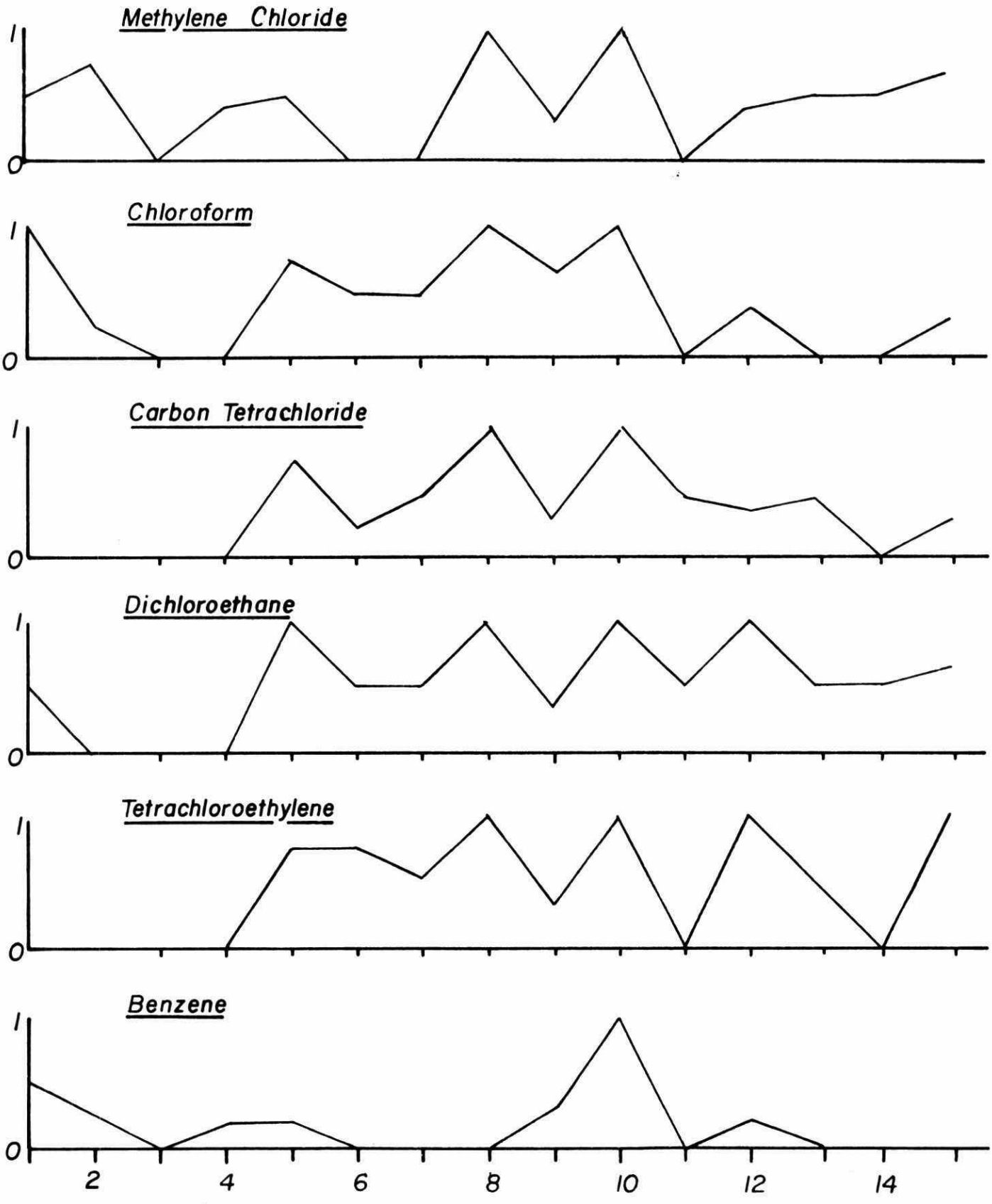


TABLE 82

Code Numbers of Sites for
Figure 12

Code #	Site	# of analyses
1	Lambton Water Supply System	2
2	River Water - Bluewater Bridge	4
3	Imperial Oil Limited - Intake	2
4	Polysar Limited - Intake	5
5	Dow Chemical - North Intake	3
6	River Water - Dow Chemical/ Sunoco Incorporated Fence Line	4
7	Sunoco Incorporated - Intake	2
8	River Water - Sunoco Below Dock	1
9	Shell Canada - Intake	3
10	River Water - Talford Creek	1
11	Allied Chemical - Intake	2
12	Private Residence Intakes	5
13	Beker Industries - Intake	2
14	Canadian Industries - Intake	2
15	River Water - Sombra Ferry Dock	3

from the #9 Separator effluent in May 1978: the levels ranged from 1 - 142 ppb but, without corresponding intake water samples, it is difficult to conclude that this effluent is a source of methylene chloride. Other chlorinated compounds were occasionally observed at trace levels. Unfortunately, only a single sample of the Bio-oxidation effluent was analyzed (Table 8, page 44): chloroform was observed at 3 ppb and benzene at 86 ppb, xylene and petroleum hydrocarbons were also present. This level of benzene may be significant and this site should be the subject of further study.

A 1975 sediment sample taken above Polysar (exact sampling site unknown) showed the highest level for solvent extractables of any on the St. Clair in 1975 (Table 61). No organics were identified in 1975. Relevant 1977 PCB samples (Figures 6 and 7 page 22) and concentrations (Tables 63 and 64, pages 100 and 101) are:

River Stations.	American Shore:	#16 (not detected), #17 (not detected), #19 (24 ppb)
	Canadian Shore:	#14 (22 ppb), #15 (not detected), #18 (21 ppb)
Industrial Stations.	#4 - #7 (not detected), #8 (19 ppb)	

The PCB results are comparable to the lowest levels encountered on the river, suggesting that they are background values. The solvent extractable value, while not specifically implicating Imperial Oil, certainly suggests that an outfall in this area (the others being Sarnia STP and Esso Chemical Canada Limited Pressure Sewer) is a major contributor of less water soluble organics to the river.

With the exception of the chlorinated methanes, which appear to be ubiquitous in the St. Clair system, the organics identified in the IOL effluents are consistent with refinery operations. The presence of the lower aromatics implies that the more hazardous polycyclic aromatic hydrocarbons (PAH's) may also be present. This should be investigated. Table 1 also shows that IOL is the third largest contributor of organics to the St. Clair, discharging approximately 1000 kg organic carbon per day.

Esso Chemical Canada Limited

Previous discussion showed that Esso's only discharge, a pressure sewer, may be of concern because of high TOC (mean 34.7 mg Carbon/liter, Table 1) and the

occurrence of aromatics. Although the TOC is quite high the low flow reduces the loading impact.

The large TOC values are consistent with the organic analyses, Table 9, which also illustrate the immense variability of industrial effluents. Samples taken on four days were analyzed (Table 9, page 45). In one case organics were only observed at low concentrations (6 ppb) but, in all other cases, at least one component reached ppm levels: this component varied and was either naphthalene, methylnaphthalene or toluene. The day-to-day variations observed for methyl-naphthalene were:

	ppm level
May 10, 1977	6 ppb
May 31, 1977 (grab)	3 ppm
June 21, 1977 (grab)	trace
July 12, 1977 (grab)	

Similar variations were apparent for other compounds. The compounds observed appear to be derived from the plants raw materials, i.e. petroleum; no product related components were observed although it is likely that most, with the possible exception of vinyl chloride monomers, are non-volatile.

The Esso sewer discharges in amongst those from Imperial Oil and hence the same sediment sites are relevant. It appears that PCB's are not generated at this plant. The high solvent extractable value obtained for the "above Polysar" site in 1975 may well be related to the high TOC and high concentration of organics in the Esso sewer since sediments tend to accumulate the less water soluble materials, e.g. aromatics.

The aromatic compounds observed are consistent with the use of petroleum products. The effectiveness of abatement equipment put into service since the time of sampling involved in this study should be examined, particularly for the less volatile aromatics, since, should these be present, the sewer presents a major hazard. While it is true that the concentrations will be diluted in the river, some aromatics tend to have a high bio-accumulation potential ("Blue Book" page 49) and the hazard will mainly be to biota in the vicinity of the outfall.

Polysar Limited

Polysar maintains a series of plants that produce polymer precursors for sale or use elsewhere in the plant. Typical precursors are benzene and derivatives (ethylbenzene, styrene) and final products include polybutadiene, polyisoprene, butyl latex and SBR/NBR co-polymers. Wastes are discharged through five sewers:

Township Ditch
54" Sewer
66" Sewer
Stereo API
72" Sewer

The Township Ditch receives used cooling water from Polysar and several smaller companies (Cabot Carbon, Fiberglas of Canada and Monsanto), plus run-off from a tank farm (Esso) and leachates from several landfill sites. A 1975 sample of the Fiberglas effluent showed low levels of chlorinated organics (Table 10) and toluene. Three of Polysar's five sewers have been implicated earlier in this Discusion: 54" Sewer, 66" Sewer and the Stereo API for high organic loading and TOC values. The 66" Sewer because of high flow is, in fact, the largest contributor of ogranics to the St. Clair (5762 kg/day, Table 1, pages 15-17). Polysar itself has the largest overall loading.

The Township Ditch, Table 11, page 47, showed fairly low levels of a variety of chlorinated compounds on occasion and, in a 1975 sample taken above Polysar, vinyl chloride at 215 ppb. An examination of the Ditch to determine the origin of these compounds seems worthwhile. 1977 samples from the 54" Sewer (Table 12, page 48) showed only trace levels of occasional organics, whereas a 1975 sample contained t-butanol at 376 ppm and vinyl chloride at 172 ppb. 1978 samples obtained over a two-day period (Table 13, page 49) showed an isolated methylene chloride level of 288 ppb, t-butanol at up to 440 ppb and a variety of sporadic aromatics and polymer precursors (butadiene, styrene, etc.) at low levels (11 ppb). The 66" Sewer again illustrated the immense variability common in industrial effluents. In 1975 and 1977 the compounds observed were mainly attributable to polymer precursors, by-products (see Discussion, page 124) etc., and were generally at quite low concentrations. A greater number of compounds were identified in the

1978 samples (Table 15, page 51), possibly because of improved methodology, and included a variety of prominent chlorinated aliphatics. The results for the Stereo API Sewer show remarkable variations. Those collected in 1975 (Table 31) and 1978 (Table 32, page 68) contained extremely high levels of aromatic hydrocarbons (1975 benzene at 149 ppm, 1978 benzene at 105 ppm) whereas the 1977 results indicated the presence of the same compounds but at much lower levels. There appears to be no explanation for this discrepancy. The high concentrations are in agreement with the 1977 TOC values (mean 77.1 mg Carbon/litre, Table 1, page 15 ff.). In 1978 both grab and automatic samples were collected and show differences the automatic samples being generally lower. It is thought that this discrepancy is due to a variable amount of headspace in the automatic samples which is particularly important at these high levels.

1977 samples for the 72" Sewer were consistent with the low TOC values (mean 5.6 mg Carbon/liter, Table 1) whereas the 1975 sample showed ppm levels of t-butanol and i-propanol. Since the 1975 study used a specific method for alcohols, which do not purge well, it is possible that they were simply not detected in 1977.

Sediment stations (Figures 6 and 7, page 22) and PCB concentrations (Tables 63 and 64, page 100 ff.) in the vicinity of Polysar are:

River Stations.	American Shore:	#21 (44 ppb)
	Canadian Shore:	#20 (75 ppb), #22 (605 ppb)
Industrial Stations.	#9, #11 (not detected), #10 (285 ppb),	
		#12 and 13 (186 ppb) and #14 (12 ppb)

These values are significantly higher than those found further upstream and imply that a sewer in this area is, or has previously been, a source of PCB's. Certain chlorinated compounds were also identified in 1975 sediment samples (Table 62, page 99). The fairly large solvent extractable values, 1.2 to 3.9 g/kg dry weight, Table 61, page 98, are consistent with the high levels of low solubility aromatics.

The majority of the organics detected in Polysar's effluents are related to their polymer operation, i.e. butadiene, styrene and other aromatics. The origin of the chlorinated compounds is not obvious and it may be that these are used as solvents. There is no doubt that most sewers need further examination to confirm

earlier results but, in the case of the Stereo API sewer, sufficient samples were analyzed to indicate that this effluent presents a serious environmental hazard. It may be, since these samples were collected in a 24-hour period, that 100 ppm levels of benzene are uncommon, and a detailed examination is recommended.

Dow Chemical Canada Limited

Dow operates a series of units on the St. Clair River which are arranged to act in conjunction producting a wide range of organic materials. In particular the plant produces styrene, glycols and derivatives, polymers, chlorine and chlorinated solvents, and caustic soda. Raw materials are brine from caverns and light hydrocarbons from other plants in the area. Dow has the largest number of sewers (nine) discharging to the St. Clair and although most have low TOC values (Table 1, pages 15-17) the sheer volume causes Dow to be the second largest contributor of organics to the river.

In earlier discussions, all Dow sewers were implicated on the grounds of possible chlorinated organic discharge and specifically: the 54" Sluice for the number of organics; the Third Street Sewer for toluene discharge, organic loading and number of organics; the Fourth Street Sewer for xylene and organic loading.

The 42" Sewer (Table 19, page 55) contained trace levels of chlorinated organics in 1977 in spite of relatively high TOC values (6 - 22.5 mg Carbon/liter, Table A6). Rather more compounds were observed in this sewer in 1975, including carbon tetrachloride at 110 ppb and trichloroethylene at 102 ppb. A reasonable conclusion from the high TOC values is that the majority of organics in this sewer are non-volatile. In 1977 a variety of organics were found in the 48" Sewer (Table 20, page 56) including carbon tetrachloride (13 ppb), dichloroethane (9 ppb) and benzene (8 ppb). Fewer compounds were observed in 1975 but carbon tetrachloride was observed at 20 ppb. These findings are consistent with the low TOC values obtained (2.5 - 5.5 mg Carbon/liter, Table A6). The Acid Tile again showed moderately high TOC values (6 - 17 mg Carbon/liter) but few organics (Table 21, page 57). A greater variety were found at trace levels in 1977 but those found in 1975 showed higher concentrations, viz. carbon tetrachloride (110 ppb) and chloroform (13 ppb). Results for the 54" Sluice are interesting: two samples collected in 1977 (one grab, one composite) contained only trace levels of various organics

whereas two grab samples (one in 1975, the other in 1977) showed fairly high levels of chlorinated compounds. In 1975, these compounds were chlorofrm (912 ppb), dichlorobromomethane (150 ppb), dibromochloromethane (66 ppb) - the ratio of these may suggest their production as by-products of aqueous chlorination - and carbon tetrachloride (1390 ppb). In 1977 dichloroethylene and dichloropropane were identified at ppm levels. This sewer certainly requires a more detailed study. The Second Street Sewer again contained chlorinated organics: in 1977 dichloroethane (168 ppb) was significant in contrast to chloroform (70 ppb), dichlorobromomethane (21 ppb) and carbon tetrachloride (13 ppb) in 1977. The Third Street Sewer results (Tables 24, 25 and 26, pages 60, 61 and 62) are quite curious: in 1975 the sewer contained carbon tetrachloride (1378 ppb) and very high levels of benzene (30 ppm), toluene (25 ppm), xylene (25 ppm) and styrene (200 ppm). In 1977 similar compounds, although more varied, were detected but concentrations of this magnitude were only observed in one grab sample: benzene (940 ppb), toluene (245 ppb), xylene (1400 ppb) and styrene (1320 ppb). It is certainly conceivable that the low values observed otherwise resulted from large head-spaces as discussed previously, although Dow have reported significant effluent improvement, indicated by TOC values, between 1975 and 1977. In May 1978, no aromatics were observed, only a variety of chlorinated compounds including methylene chloride (1-118 ppb) and carbon tetrachloride (not detected to 250 ppb). In October 1978, the aromatics present were at high levels and were quantitated by Direct Aqueous Injection: chlorinated compounds were not observed. As a result of an incident these samples contained high (3 ppm) levels of the aromatics observed previously. In some cases the aromatic levels were so high that distinct organic/water layers formed. This hampered the analyses and implies that the levels presented in Table 26 are probably underestimates. While concentrations observed following the incident may not be representative, they demonstrate the enormous effect of industrial incidents.

The DOEO (Table 27, page 63) Sewer had low TOC values (2 - 5 mg Carbon/liter, Table A6, page 179) and correspondingly low organics: methylene chloride (47 ppb, 1977), carbon tetrachloride (15 ppb, 1975) and t-butanol (3 ppm, 1975). t-Butanol is easily bio-degraded and not regarded as especially significant.

Dow Fourth Street Sewer showed high organic loading (Table 1, pages 15-17) but this mainly arises because of the high flow rates. A variety of organics - again

chlorinateds and aromatics - were detected (Table 28, page 64); the most significant being carbon tetrachloride (100 ppb) in 1975.

The Steam Plant sewer (Table 29, page 65) showed a high level of t-butanol (3 ppm) in 1975 but otherwise only low levels of chlorinated compounds (16 ppb). This is in keeping with the low TOC values (2.5 - 6 mg Carbon/liter, Table 16, page 52).

Sediment samples (Figures 6 and 7) and PCB concentrations (Tables 63 and 64, pages 100 and 101) in the vicinity of Dow are:

River Stations.	American Shore:	#23 (70 ppb)
	Canadian Shore:	#22 (605 ppb), #24 (3370 ppb)
		(Sample 22 is slightly upstream of Dow)
Industrial Stations.	#15 (11 ppb), #16 and 17 (10,000 ppb)	
		#18 (2280 ppb), #19 (368 ppb)

Sediment Analysis performed on sediment samples collected in 1975 showed a variety of chlorinated organics; approximation quantitation was performed for one sample and suggested the levels were as high as 400 ppm (Table 62, page 99). The solvent extractable values (Table 61, page 98) again suggest the release of relatively water insoluble materials. At the time of writing, the results of GC/MS analyses on samples extracted and fractionated by Dr. R. D. Smillie, OTC Section, have become available. While these analyses were purely qualitative, high levels of PCB's (confirmed by this GC/MS analysis), aromatics (diphenylether, biphenyl, methylbiphenyl and diphenylmethane) and PAH's (anthracene, pyrene, fluoranthene, benzanthracene, benzopyrene, carbazole and derivatives) were observed.

The variety of compounds observed in the vicinity of Dow are clearly related to the polymer (aromatic organics) and chlorinated compound production.

Sunoco Incorporated

Sunoco maintains a refinery operation on the St. Clair River capable of processing 90,000 barrels/day. Waste material is discharged via a single sewer.

In previous discussion it was indicated that this effluent showed low TOC, organic loading and number of organics. The only area of potential concern might be the presence of tetrachloroethylene although the proximity of this operation to the discharges of Dow, where chlorinated compounds are common, suggests that carry-over might be occurring. The TOC values measured (3.5 to 10 mg Carbon/liter, Table A8, page 181) are indeed low and consistent with the organics observed (Table 30, page 66). Initial screening in 1975 revealed only trace levels and the sample was not analyzed further. The sample analyzed in 1977 contained trace levels of several organics, all chlorinated, but as several (chloroform, dichloroethane, tetrachloroethylene and bischloroisopropylether) were also observed at similar levels in the intake water (Table 49, page 86), the conclusion that these compounds originate upstream is inescapable.

Relevant sediment sites (Figures 6 and 7, page 22) and PCB concentrations (Tables 63 and 64, page 100 ff.) are:

River Stations.	American Shore:	#27 (98 ppb)
	Canadian Shore:	#24 (3370 ppb), #26 (135 ppb), #28 (137 ppb) (With the exception of #24 these are quite far downstream of Sunoco)
Industrial Stations.	#20 (80 ppb)	

The solvent extractable value obtained at a site below Dow was very low (240 mg/kg dry weight, Table 61, page 98) and the only organics identified at this site (Table 62, page 99) were aliphatic hydrocarbons. Although the PCB values obtained in the vicinity of Sunoco were high it is difficult to conclude whether this implicates Sunoco, since the values obtained upstream are also high. From the rather limited evidence presented it appears that Sunoco's operation does not present much environmental concern although this might be confirmed in another study.

Shell Canada Limited

Shell operates a refinery on the St. Clair River with a capacity of 90,000 barrels/day. Water is drawn directly from the river but wastes are discharged

through two sewers to Talford Creek. Since at times the company's discharge constitutes the majority of the flow in the Creek, the River Water, Talford Creek, results are also relevant here. One of the two sewers is used to discharge used cooling ("clean") water while the other receives process wastes ("contaminated").

Both sewers have shown, from early discussion, the potential for discharging chlorinated compounds although other criteria suggested no significant hazard. The TOC and loading figures (Table 1, page 15 ff.) were low in 1977. The clean water sewer, Table 31, page 67, showed trace levels of four compounds two of which, dichloropropane and benzene, were identified at similar levels in the intake water. Rather more compounds were observed in the contaminated water sewer but none were observed in excess of 12 ppb (methylene chloride). Once again, two of the compounds were observed in the intake water. The Talford Creek sample (Table 52, page 89) showed rather higher levels of organics than either of Shell's sewers but none exceeded 9 ppb (chloroform).

Relevant sediment samples (Figures 6 and 7, page 22) and PCB concentrations (Tables 63 and 64, page 100 ff.) are:

River Stations.	American Shore:	#33 (9 ppb), #35 (17 ppb)
	Canadian Shore:	#30 (275 ppb), #32 (53 ppb)
		(Station 30 is slightly upstream of Shell)
Industrial Stations.	#21 (348 ppb)	

Solvent extractable values were low by the Shell Dock (437 mg/kg dry weight) and somewhat higher at the mouth of Talford Creek (1530 mg/kd dry weight, Table 61, page 98).

As with Sunoco, significant PCB levels were found in sediments from the vicinity of Shell Canada but the remainder of the evidence indicated that the organic discharge is of minimal significance. It appears that the majority of organics observed again originate upstream. It is interesting that product-related organics (i.e. aliphatics and aromatics) were not observed at this site. This may well reflect abatement improvements made since 1968 as oil discharges were a major concern at that time.

Ethyl Corporation of Canada Limited

The Ethyl plant is mainly concerned with the production of alkyl lead compounds and lead scavengers (dichloroethane) for use in gasolines. Part of the plant produces pharmaceuticals which contribute little to the discharge. Waste materials are discharged via a single sewer.

In the earlier discussion, it was shown that possible concern might arise from the discharge of dichloroethane. TOC values were low (3-10 mg Carbon/liter, Table A10) as was organic loading. The organic results (Table 33, page 69) indicated the presence of a variety of chlorinated organics with certain compounds occasionally reaching ppm levels. This occurrence appears quite frequent, viz 1,2-dichloroethane 1 ppm in 3 out of 5 samples; chloroethane, trichloroethane, 1,2-dibromoethane and trichlorobutane 1 ppm on 1 out of 5 samples. The sample collected on May 10, 1977, was curious in that the only component identified was dichloroethane at trace levels.

Sediment sampling sites (Figures 6 and 7, page 22) in the vicinity of Ethyl and the PCB concentrations (Tables 63 and 64, page 100 ff.) are:

River Stations.	American Shore:	#33 (9 ppb), #35 (17 ppb)
	Canadian Shore:	#32 (53 ppb), #34 (646 ppb)
		(Station 32 is slightly upstream of Ethyl's discharge; #34 is downstream close to DuPont
Industrial Station.	#22 (395 ppb)	

Although the PCB concentrations seem to be generally quite high along the Canadian bank downstream of Dow, there is a sharp increase at station 34 (646 ppb) that implicates Ethyl as another past or present PCB source. This would seem to correlate quite well with the discharge, frequently very high, of chlorinated compounds. Clearly, this effluent may present an environmental hazard.

DuPont Canada Incorporated

The DuPont plant produces polyethylene from locally obtained ethylene. The operation is such that discharge through the single sewer is generally clean, at least visually, although polymer pellets are occasionally observed.

The only possible concern suggested previously was the frequent occurrence of dichloroethane in this discharge. The TOC values and net organic loading (calculated assuming an intake value of 4 mg Carbon/liter) are both low (Table A10). The analytical results indicated the frequent presence of chlorinated compounds, particularly methylene chloride (5-10 ppb) and dichloroethane (4-163 ppb), and benzene and toluene on isolated occasions (Table 34, page 70).

Relevant sediment sites (Figures 6 and 7, page 22) and PCB concentrations (Tables 63 and 64, page 100 ff.) are:

River Stations.	American Shore:	#35 (17 ppb)
	Canadian Shore:	#34 (646 ppb)
Industrial Stations.	#23 (130 ppb), #24 (270 ppb)	

A 1975 sediment sample downstream of DuPont showed a quite high solvent extractable value (4010 mg/kg dry weight, Table 61, page 98).

It is unfortunate that DuPont Intake water samples were not obtained in 1977. This portion of the river, in the vicinity of Stag Island, has several industries close to one another, i.e. Ethyl, DuPont and Petrosar. The organics detected in the DuPont effluent were similar to those observed at much higher levels in the Ethyl discharges suggesting that their origin is upstream. The location of the sediment samples makes it difficult to pinpoint a source of PCB's but, in view of the quite dramatic jump at site #34, it seems likely that there is one in this area. It seems reasonable to conclude that DuPont's operation is essentially clean although confirmation of the presence of chlorinated compounds in the intake water seems desirable.

Petrosar Limited

No Petrosar samples were analyzed for organic compounds. The design of the refinery is such that water usage is minimized and the wastes well dispersed (see Background Information).

The TOC values, summarized in Table 1, suggest that the organic contribution to the river is fairly low.

Union Carbide Canada Limited

This plant was in the process of completion during the 1977 study and as a result, neither TOC nor organic analyses were performed.

Since the plant, like DuPont, is concerned with the production of polyethylene organic discharges are likely to be minimal, and limited to occasional polymeric material.

Allied Chemical Canada Limited

The Allied plant (now closed down) in 1977 was producing toluene di-isocyanate for use in a variety of polyurethane formulations. Wastes are discharged via a single sewer.

Possible concerns identified earlier were the number of organics and discharge of carbon tetrachloride and xylene. The TOC values and loadings, Table 1, indicate a very low contribution of organic material to the river. Nevertheless, a variety of chlorinated compounds, aromatics and chloroaromatics were observed (Table 35, page 71). In 1975, chloroform (202 ppb) and carbon tetrachloride (981 ppb) were the only organics identified. 1977 analyses showed consistent concentrations of a variety of compounds, most significant being carbon tetrachloride (trace to 66 ppb), dichloroethane (trace to 37 ppb), dichlorobenzenes (trace to 138 ppb) and trichlorobenzenes (trace to 80 ppb). It appears that Allied was certainly a source of chlorinated benzenes since these compounds, unlike the others, were not detected upstream. The intake water samples showed only carbon tetrachloride (1975) and dichloroethane (1977).

Sediment samples (Figures 6 and 7, page 22) in the vicinity of Allied and the corresponding PCB concentrations (Tables 63 and 64, page 100 ff.) are:

River Stations.	American Shore:	#39 (125 ppb), #43 (18 ppb)
	Canadian Shore:	#40 (38 ppb), #41 (95 ppb), #42 (174 ppb)
Industrial Stations.	#26 (68 ppb), #27 (104 ppb), #28 (not detected) (Stations #41 to 43 and #28 are quite far downstream)	

A 1975 solvent extractable value obtained for a sample downstream of Allied (Table 61) was high at 5206 mg/kg dry weight although no volatile organics were identified. This suggests a source of water-insoluble compounds in the vicinity of Allied and is consistent with the discharge of aromatics. There also appears to be a source of PCB's in the area. The observation of chlorobenzenes is also interesting since these were otherwise only observed at Dow and in Water Quality samples downstream of Allied. Thus it appears that Allied, despite low TOC values, contributed significant organics to the river although, once again, upstream origin cannot be excluded.

Beker Industries of Canada Limited

Beker produced ammonia for use in fertilizers. Plant wastes were discharged via two sewers, one handling process wastes (API) and the other used cooling water.

Potential problem areas were discharge of chlorinated compounds from the used cooling water, quite likely carry-over, and dichloroethane and xylene from the API sewer. The TOC and organic loading were clearly low (Table 1). The organics observed (Table 36, page 72) were chlorinated hydrocarbons and aromatics: most were of low concentration with the exception of xylene (290 ppb) in the API sewer.

Relevant sediment sites (Figures 6 and 7, page 22) and PCB concentrations (Tables 63 and 64, page 100 ff.) are:

River Stations. Canadian Shore: #53 (68 ppb)
Industrial Stations. #30 (47 ppb), #31 (20 ppb)
(Site #30 is upstream of Beker)

1975 solvent extractable analyses indicated low values in sediments from the vicinity of Beker, no organics were identified.

It seems, again, highly likely that the majority of compounds observed at Beker originate upstream especially as chlorinated compounds were observed in the intake water.

Canadian Industries Limited

This plant, like Beker, is mainly concerned with the production of ammonia and inorganic fertilizer. Wastes are discharged via a single sewer.

The CIL operation is essentially clean with regard to organics. Both TOC and organic loading values are low (Table 1). The organic analysis (Table 37) showed only trace levels of the lower chlorinated organics although several were detected in a 1975 in-plant sample.

Sediment samples (Figures 6 and 7, page 22) and PCB concentrations (Tables 63 and 64, page 100 ff.) in the vicinity of CIL are:

River Stations.	American Shore:	#55 (122 ppb)
	Canadian Shore:	#54 (98 ppb), #56 (556 ppb)
Industrial Stations.	#32 (152 ppb)	

Solvent extractables were low and no organics were identified in 1975.

The PCB data appears to indicate a source in the vicinity of CIL: this is difficult to explain in light of the chemical operation.

ii) Sewage Treatment Plant Effluents

Three sewage treatment plant final effluent samples were analyzed: the results are presented in Tables 38, 39 and 40, page 74 ff. All showed low ppb concentrations of chlorinated aliphatics. Since some of these are known to be produced during aqueous chlorination their occurrence is not unreasonable. Others, for example dichloroethane, tri- and tetrachloroethylene in Sarnia STP, may well arise from industrial sources. The only anomaly in these results is the observation of high ppm, concentrations of aromatics in the Point Edward effluent. This is believed to have an industrial origin - either spillage or dumping - and requires further study to determine the frequency with which this can occur.

iii) Samples Indicating Water Quality

These results have, to an extent, been examined previously in the discussion, and the distribution of organics bears a striking resemblance to the effluents (Figures 9, 10, 11 and 12). The organic analytical data is presented in Tables 41 to 57.

The major conclusion that is apparent from the organic data is that the quality of the river water samples is remarkably good, especially when the vast quantity of industrial effluent discharged to the river is considered. In the following discussion only the unusual results are addressed.

One sample of the Lambton Water Supply System finished water showed a high (95 ppb) level of methylene chloride. There appears to be no obvious explanation for this level since this site is above the industrial plants. Possible explanations include depuration of dredge spoils, aerial transport and industrial activity within the Lake Huron Basin. Eight repeat samples (four of raw water and four of treated water) collected on different days early in 1980 showed low levels of methylene chloride (5 ppb) and are far more in line with other treatment plants (cf. Routine Monitoring data Tables 71, 72 and 73, page 108 ff.).

Dow Chemical's North Intake contained 3 ppm of t-butanol in 1975 (none was found in 1977). Although this level is high it is not considered hazardous because of the bio-degradability of alcohols. Dow's South Intake contained 67 ppb of carbon tetrachloride in 1975 which is presumably related to the Dow operation since this compound was frequently observed in Dow effluents. River water samples from below Dow (Table 48) frequently contained many of the compounds observed in Dow's effluents.

One 1975 sample from the Shell Canada Intake (Table 51) contained carbon tetrachloride at 91 ppb which, again, may be related to Dow's effluents.

The private water supplies, Table 54, contained a variety of chlorinated organics at low levels (20 ppb), including dichlorobenzene. The latter compound was only observed in Water Quality samples below Allied Chemical, apparently confirming Allied as a source of this compound.

The 1977 sample from Beker Industries intake water contained methylene chloride at 50 ppb. Again no explanation is obvious.

iv) Samples Dependent on Water Quality

As described previously, two types of sample fall into this category, fish and bottom sediments. Sediment data has already been discussed in relation to the Industrial Effluents and so the following will be restricted to the fish data.

Unfortunately, no data is available on fish size, age or exact site of capture which somewhat limits the conclusions that can be drawn. All fish samples analyzed showed the presence of hydrocarbons, often at very high levels, which tends to have two effects on the analyses. Firstly, it restricts the amount that can be purged since oil causes foaming which can, if care is not taken, reach the Tenax trap. Secondly the hydrocarbon envelope tends to obscure the presence of other compounds, particularly if they are present at low levels. This may account for the fact that chlorinated compounds were not observed in fish from the St. Clair River.

Aromatic hydrocarbons were detected in all fish analyzed although quantitation was not always possible, for the reasons given above. Compounds of this class are known to have a high bio-accumulation potential as is illustrated by comparing the results with those for the industrial effluents. There were no obvious variations with species (Table 60) although the database is rather limited.

These results confirm that discharge of organics can present an environmental hazard, even when they are present at low levels, because the bio-accumulation potential may be large. Further discussion is contained in the Report on Fish Tainting and Toxicity (due to be released in Fall 1980).

v) Other Samples

Results discussed here are, as mentioned previously, obtained from samples not taken directly from the St. Clair River but rather from connected bodies of water (i.e. Lake Huron, Lake St. Clair, the Detroit River, etc.).

The results for Wallaceburg STP Raw Sewage and Final Effluent (Table 65) are quite similar to those for STP's on the St. Clair itself. A variety of low level chlorinated and aromatic compounds were observed. The highest concentrations observed (5-15 ppb) were for chloroform and, as the level of chlorinated compounds

was generally higher in the effluent than in the raw sewage, this provides further evidence for the occurrence of aqueous chlorination.

Data from the Little River STP, Table 66, and West Windsor STP, Table 67, are quite different to others examined. Both show high (ppm) levels of organics in the raw sewage: dimethyl disulphide in both cases and diethylbenzenes in Little River. The difference is that the dimethyl disulphide remained in the West Windsor effluent but was absent from the Little River effluent. The diethylbenzene was also not observed in the Little River effluent. The Little River STP is in a heavily industrialized area and it seems likely that aromatics are being discharged to the sewer system but that they are effectively handled by the plant, which employs secondary treatment. In contrast, West Windsor is a primary plant, i.e. without aeration, which seems to account for the high dimethyl disulphide. Chlorinated compounds were also present in the West Windsor, but not the Little River, effluent.

Samples from the Walpole Island Water Treatment Plant contained quite significant levels (60 ppb) of chlorinated compounds and aromatics (Table 68). Unfortunately, no intake water samples were obtained so the origin of these compounds is uncertain and requires further examination.

Finished water from the A. J. Brian Pumping Station, Table 69, was generally of good quality although methylene chloride was observed at 37 ppb.

The only fish sample taken from Lake Huron, Table 70, was remarkably low in organics, whereas those from Lake St. Clair showed similar results to samples from the St. Clair River.

In general, fish from Lake St. Clair showed lower concentrations than those from the St. Clair River although the same type of compounds, i.e. aromatics, were detected. It appears, largely on the basis of the single sample from Lake Huron, that the effects of the Industrial operations on the St. Clair are very obvious on the fish. One sample from Tremblay Creek, Lake St. Clair, contained 330 ppb tetrachloroethylene; again this is apparently related to the industrial operations.

Tables 71, 72 and 73 present considerable quantities of data from routine monitoring analyses for haloforms, carbon tetrachloride and trichloroethylene from sites where water is taken from Lake St. Clair and the Detroit River. In general, the Tilbury North samples, where water is taken from Lake St. Clair, have lower concentrations than the others. Raw water concentrations are invariably less than finished water, i.e. aqueous chlorination is implicated. Carbon tetrachloride is not, apparently, produced this way as it is never found in the finished water only. It would seem that this compound arises from industrial operations. The higher levels in samples where Detroit River water is used do not necessarily represent activity on the St. Clair River since the Detroit/Windsor areas are also heavily industrialized. Furthermore, the concentration of chlorinated compounds may arise either from the compounds themselves or from high levels of precursors, i.e. compounds that form chloroform, etc. on aqueous chlorination.

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Appendix 1

Industrial Effluent TOC, Flow and

Organic Loading

Data

Tables A1 - A15

TABLE A1

Imperial Oil Limited - Discharge Data

	Flow (min-max) 1000's m^3/day)	TOC (mg Carbon/L) min.	max.	mean
#3 Separator	54.6 - 68.2	2.0	5.0	3.0
#9 Separator	54.6	4.0	18.0	8.4
#11,12 Separator*	54.6	3.5	8.0	5.8
Bio-oxidation (BIOX)*	13.6 - 31.8	13.5	62.0	26.7
Intake	--	2.0	3.0	2.6

Total discharge: 177,400 - 209,200 m^3/day

* Discharge through common outfall

TABLE A2

Imperial Oil Limited

Discharge of Organic Carbon (kg/day)

	Min. Loading	Max. Loading	Mean Loading
#3 Separator	109.2	341.0	184.2
#9 Separator	218.4	982.8	454.8
#11,12 Separator	191.1	436.8	314.0
BIOX	183.6	1971.6	605.4
TOTAL	702.3	3732.2	1558.4
Intake	354.8	717.6	537.4
Net Organic Carbon Discharged	347.5	3014.6	1021.0

Calculated as described on page 8

TABLE A3

Esso Chemical Canada Limited
Discharge and Organic Loading Data

Pressure Sewer	Minimum	Maximum	Mean/Avg.
Discharge rate ($1000\ m^3$/day)	9.1	13.6	11.4
TOC values (mg Carbon/liter)	13.0	84.0	34.7
Discharge of Organic Carbon (kg/day)	118.3	1142.4	395.1

Organic discharge data calculated as described previously (page 8)

TABLE A4

Polysar Limited - Discharge Data

	Flow (min-max) ($1000\ m^3$/day)	TOC (mg Carbon/L) min.	max.	mean
Township Ditch	245.5	2.5	9.0	5.6
54" Sewer	63.6 - 81.8	9.5	49.0	29.6
66" Sewer	259.1 - 331.9	18.0	33.0	24.8
Stereo API	2.7	69.0	89.5	77.1*
72" Sewer	15.9 - 20.0	3.0	9.0	5.6
Intake	--	4.0	7.0	5.3

Total discharge 586,800 - 681,900 m^3/day
* Mean of five values

TABLE A5

Polysar Limited
Discharge of Organic Carbon (kg/day)

	Min. Loading	Max. Loading	Mean Loading
Township Ditch	613.8	2209.5	1374.8
54" Sewer	604.2	4008.0	2151.9
66" Sewer	4663.8	10952.7	7337.3
Stereo API	186.3	241.7	208.2
72" Sewer	47.7	180.0	100.2
TOTALS	6115.8	17591.9	11172.4
Intake	2347.2	4773.3	3330.3
Net Organic Carbon Discharged	3768.6	12818.6	7842.1

Figures calculated as
described on page 8

TABLE A6

Dow Chemical Canada Limited
Discharge Data

	Flow (min-max) (1000's m^3/day)	TOC (mg Carbon/L) min.	max.	mean
42" Sewer	41.8 - 69.1	6.0	22.5	10.2
48" Sewer	67.7	2.5	5.5	3.6
Acid Tile	12.3	6.0	17.0	12.7
54" Sluice	35.0	2.5	18.0	7.3
Second Street	52.7	11.0	20.0	15.8
Third Street	130.9	10.5	15.5	13.6
DOEO	100.9	2.0	5.0	3.3
Fourth Street	263.7 - 313.7	6.0	13.5	8.1
Steam Plant	17.3	2.5	6.0	3.8
Intake	--	1.5	5.0	3.3

Total discharge: 722,300 - 799,600 m^3/day

Data supplied by T. E. Wood, Sarnia Regional Office

TABLE A7

Dow Chemical Canada Limited
Discharge of Organic Carbon (kg/day)

	Min. Loading	Max. Loading	Mean Loading
42" Sewer	250.8	1554.8	565.6
48" Sewer	169.3	372.4	243.7
Acid Tile	73.8	209.1	156.2
54" Sluice	87.5	630.0	255.5
Second Street	579.7	1054.0	832.7
Third Street	1374.5	2029.0	1780.2
DOEO	201.8	504.5	333.0
Fourth Street	1582.2	4235.0	2338.5
Steam Plant	43.3	103.8	65.7
TOTALS	4362.9	10692.6	6571.1
Intake	1083.5	3998.0	2511.1
Net Organic Carbon Discharged	3279.4	6694.6	4060.0

Figures calculated as
described on page 8

TABLE A8

Sunoco Incorporated
Discharge and Organic Loading Data

	Minimum	Maximum	Mean/Avg.
Flow ($1000\ m^3$/day)	--	--	68.2
TOC (mg Carbon/liter)	3.5	10.0	6.3
Intake TOC (mg Carbon/liter)	2.0	6.0	3.9
Total Organic Carbon Discharged	238.7	682	429.7
Total Organic Carbon Intake	136.4	409.2	266
Net Organic Carbon Discharged	102.3	272.8	163.7

Loading data calculated as
described on page 8

TABLE A9

Shell Canada Limited
Discharge and Organic Loading Data

	Flow ($1000\ m^3$/day)	TOC (mg carbon/liter) min.	max.	mean
Contaminated Water	100.0	4.0	6.5	5.6
Clean Water	120.9	1.0	8.0	3.8
Intake	--	0.5	5.5	3.2

Total Discharge: 220,900 m^3/day

Organic Carbon Loadings (kg/day)

	Min.	Max.	Mean
Contaminated Water	400.0	650.0	560.0
Clean Water	120.9	967.2	459.4
TOTALS	520.9	1617.2	1019.4
Intake	110.5	1215.0	706.9
Net Organic Discharge	410.4	402.0	312.5

Figures calculated as described on page 8

TABLE A10

Ethyl Corporation of Canada Limited
Discharge and Organic Loading Data

	Min.	Max.	Mean/Avg.
Flow ($1000\ m^3$/day)	34.5	44.1	39.3
TOC (mg Carbon/liter)	3.0	10.0	5.3
Total Organic Carbon Loading	103.5	441.0	208.3

Organic loading data calculated as described on page 8

TABLE A11

DuPont Canada Incorporated
Discharge and Organic Loading Data

	Min.	Max.	Mean/Avg.
Flow ($1000\ m^3$/day)	--	--	27.3
TOC (mg Carbon/liter)	3.0	8.0	6.3
Organic Carbon Loading (kg/day)	81.9	218.4	172.0

Organic loading calculated as described on page 8

TABLE A12

Petrosar Limited
Discharge and Organic Loading Data

	Average Value
Flow (1000 m^3day)	22.8
Discharge TOC (mg Carbon/liter)	7.8*
Intake TOC (mg Carbon/liter)	3.3*
Total Organic Carbon Discharged (kg/day)	176.2
Total Organic Carbon Intake in (kg/day)	73.9
Net Organic Carbon Discharged (kg/day)	102.3

* Average of two values

Organic loadings calculated as
described on page 8

TABLE A13

Allied Chemical Canada Limited
Discharge and Organic Loading Data

	Min.	Max.	Mean/Avg.
Flow (1000 m^3/day)	--	--	16.4
Discharge TOC (mg Carbon/liter)	0.5	8.0	4.2
Intake TOC (mg Carbon/liter)	3.0	8.0	4.5*
Discharge Organic Carbon (kg/day)	8.2	131.2	68.9
Intake Organic Carbon (kg/day)	49.2	131.2	73.8
Net Organic Loading (kg/day)	-41.0	-5.1	

* Mean of five values

Organic loadings calculated as
described on page 8

TABLE A14

Beker Industries of Canada Limited
Discharge and Organic Loading Data

	Min.	Max.	Mean/Avg.
Cooling Water			
Flow ($1000\ m^3$/day)	--	--	81.8
TOC (mg Carbon/liter)	1.5	9.0	3.8
Organic Carbon Discharged (kg/day)	122.7	736.2	310.8
API Sewer			
Flow ($1000\ m^3$/day)	--	--	0.9
TOC (mg Carbon/liter)	2.0	11.0	6.6
Organic Carbon Discharged (kg/day)	1.8	9.9	6.0
Intake			
TOC (mg Carbon/liter)	1.5	4.0	2.3
Total Discharge: $82{,}700\ m^3$/day			
Total Organics Discharged (kg/day)	126.5	746.1	316.8
Intake Organics (kg/day)	124.1	330.8	190.2
Net Organics Discharged (kg/day)	2.4	415.3	126.6

Organic loadings calculated as described on page 8

TABLE A15

Canadian Industries Limited
Discharge and Organic Loading Data

	Min.	Max.	Mean/Avg.
Flow (1000 m^3/day)	--	--	322.8
TOC (mg Carbon/liter)	1.0	5.0	2.8
Intake TOC (mg Carbon/liter)	1.5	3.0	2.8
Organic Carbon Discharged (kg/day)	322.8	1613.8	913.5
Organic Carbon Intake (kg/day)	484.2	968.4	887.7
Net Organic Carbon Discharged (kg/day)	-161.4	645.4	25.8

Organic loadings calculated as
described on page 8

Appendix 2

Toxicological Data on Some of the Components Identified in the St. Clair River

The following data was compiled by Drs. Harding and Fitch of the Special Studies and Services Branch, Occupational Health and Safety Division of the Ministry of Labour.

1,2-DICHLOROETHANE

(also known as ethylene dichloride or EDC)

Acute Toxicity

LC_{50} rats is 48,600 mg/m^3 for 32 minutes.

LC_{50} rats is 4,048 mg/m^3 for 432 minutes.

Acute effects consist of narcosis, pulmonary edema, headache, necrotic and hemorrhagic lesions of the liver and kidney and internal bleeding. Repeated exposures can bring on nausea, vomiting, stomach pain, irritated mucous membranes, loss of appetite and liver and kidney failure.

Chronic Toxicity

In rats, guinea pigs, rabbits and cats, there were no apparent effects after receiving 400 mg/m^3 for 17 weeks for 6 hrs/day, 5 days/week.

Dogs exposed to 1,000 ppm for 7 hours developed clouding of the cornea which was reversible on cessation of exposure. This effect has not been observed in man.

Toxicity in Man

Odor threshold is 50 ppm. At 100-200 ppm the odor is not unpleasant.

High concentrations (not stated) will cause stupor, mental confusion, nausea and vomiting and C.N.S. depression. All are reversible on cessation of exposure.

Injestion of 1-2 oz has been fatal in male adults. When 1,2-dichloroethane is ingested, the predominant characteristic is blood disorders, including clotting problems. With skin absorption or inhalation, the first effects are headache, weakness, eye irritation, cyanosis and nausea.

Two cases of chronic exposure in man have been reported:

1. After 9 weeks of using 1,2-dichloroethane as a solvent, a worker developed weight loss, drowsiness, nervousness, nausea and vomiting.

2. After 5 months, a worker developed upper abdominal pain, tremor of the tongue, nausea and vomiting. All symptoms in both cases disappeared after removal from exposure.

Numerous cases of 1,2-dichloroethane poisoning, both fatal and non-fatal, have been documented by the National Institute for Occupational Safety and Health.

Experimental Work

There have been recent important findings concerning carcinogenic properties of 1,2-dichloroethane in animals and in the Ames test.

1,2-dichloroethane is weakly mutagenic in salmonella typhimurium TA 1530 and TA 1535 strains and non-mutagenic for TA 1538 strain. It could not be activated to a more mutagenic form using standard rat liver S-9 mix.

1,2-dichloroethane has been reported as mutagenic in Drosophila. An eight-hour treatment increased the frequency of recessive lethals. Twenty-four hour contact produced 25-30% mutations which were more pronounced in males. One hour contact produced 2-6% mutations.

The findings of a recent National Cancer Institute study on the carcinogenesis of 1,2-dichloroethane were released on September 26, 1978.

1,2-dichloroethane was administered to rats and mice by gastric intubation 5 times a week for 78 weeks following which, they were observed for the remainder of their life time. The high dose given had previously been found to be compatible

with a normal life span. The low dose was half of this. The dosing levels were as follows:

low dose 50 mg/kg of body wt. for rats
high dose 100 mg/kg of body wt. for rats
low dose 100 mg/kg of body wt. for male mice
high dose 200 mg/kg of body wt. for male mice
low dose 150 mg/kg of body wt. for female mice
high dose 300 mg/kg of body wt. for female mice.

Their conclusion states that, under the test conditions, 1,2-dichloroethane is carcinogenic to rats and mice, causing cancers of stomach, spleen and other organs, and subcutaneous cancers in male rats, mammary cancers in female rats and mice, uterine cancers in female mice and lung cancers in both male and female mice.

The current threshold limit value for 1,2-dichloroethane is 50 ppm (200 mg/m^3) but a reduction to 10 ppm (40 mg/m^3) TWA has been proposed by the ACGIH. This value may be changed again when the carcinogenic study results are taken into consideration.

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1,1-DICHLOROETHANE

(Little information is available on this compound)

Rats, guinea pigs, rabbits and cats tolerated inhalation of 500 ppm for 13 weeks without adverse effects. The rat, guinea pig and rabbit then tolerated an increase to 1,000 ppm for 13 additional weeks, but in the cat, this level resulted in kidney damage.

Using 1,2-dichloroethane, the highest dose tolerated was 100 ppm for 17 weeks.

It is judged that 1,1-dichloroethane is about 5 times less toxic than 1,2-dichloroethane.

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1,2-DIBROMOETHANE

(also known as ethylene dibromide or EDB)

Toxicity

1,2-dibromoethane is an extremaly strong irritant. Chronic exposure results in liver and kidney damage. High levels of exposure cause immediate CNS depression

and usually death in laboratory animals. At 200 ppm in air, laboratory animals survive for only a few hours and adverse effects have been noted at 30 ppm. Domestic animals have shown severe reproductive effects following exposure.

In humans, weakness and rapid pulse have been associated with exposure and, less commonly, cardiac failure leading to death.

Experimental Findings

1,2-dibromoethane is mutagenic and teratogenic in animals.

In 1974, NCI issued a memorandum of alert citing preliminary findings of strong carcinogenicity in rats and mice. They observed a high incidence of squamous cell carcinoma of the stomach in both rats and mice, with tumors observed after 6 weeks of exposure.

Ames testing procedures have shown 1,2-dibromoethane to be mutagenic (without metabolic activation) in Salmonella typhimurium TA 1530 and TA 1535 strains. The mutagenic property was more active than the weakly mutagenic 1,2-dichloroethane.

1,2-dibromoethane shows a pronounced mutagenicity in Drosophila.

National Cancer Institute has very recently (November 1978) issued their final report on the carcinogenicity of 1,2-dibromoethane.

Their study was conducted in a similar fashion as for 1,2-dichloroethane, described above, and their conclusion is that 1,2-dibromoethane is a strong carcinogenic agent in rats and mice.

The threshold limit value lists 1,2-dibromoethane as a potential human carcinogen awaiting reassignment of a threshold limit vale pending further data acquisition. Under this heading, no exposure or contact by any route - respiratory, skin or oral, as detected by the most sensitive methods - shall be permitted. "No exposure or contact" means hermitizing the process or operation by the best practicable engineering methods. The worker should be properly equipped to ensure virtually no contact with the carcinogen.

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HEXACHLOROBUTADIENE (HCBD)

A by-product of certain processes associated with the chlorination of hydrocarbons (i.e. the production of perchlorethylene, trichloroethylene and carbon tetrachloride) was found as a component of the tarry waste.

In 1976, it was reported from Dow Canada that its appearance was in the waste products which are re-cycled or incinerated. Some is disposed in an impervious underground cavern or approved landfill site as an interim measure.

Concentrations in chlorinated products is well below 1 ppm.

Stated that it will be gradually photodegradable.

Animal Studies

A representative series (ref) of rodent studies is presented. Other references will be made available later.

Acute Toxicity - Moderate Toxicity

LD_{50} 200-300 mg/kg for a single oral dose in rats. In a 30-day toxicity study, rats received HCBD in the diet at daily doses of 1 to 100 mg/kg. Renal toxicity (renal tubal degradation, necrosis, regeneration and increased kidney weight) was observed at doses of 30, 65 and 100 mg HCBD/kg/day.

Chronic Toxicity

Rats on diets of 20, 2.0 or 0.2 mg/kg/day of HCBD for up to 24 months were compared with control groups. Renal toxicity was observed at the intermediate and high dose levels, and at the highest dose level of 20- mg/kg/day, renal tumors (adenemas and metastasing adenocarcinomas) were seen.

Reproductive Studies

Male and female rats on diets of 1, 0.2, 2.0 and 20 mg/kg/day for 90 days prior to mating and, subsequently, through gestation and lactation showed toxicity at the two higher dose levels comprising alterations in the kidney as well as decreased weight gain and food consumption, but there was no effect on percent pregnancy, neonatal survival and development. The body weight of pups at weaning (21 days old) was slightly but significantly less than that of control litters.

In another study, neonatal rats were more sensitive to the lethal effect of HCBD than adult rats: LD_{50} adult rats - single oral dose = males 580 mg/kg and females 200-400 mg/kg. 21-day old rats - single oral does = males 65 mg/kg and females 46 mg/kg.

No information is available on human toxicity.

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XYLENES (DIMETHYLBENZENES)

Used in industry, "xylene" refers to a mixture of o-, m- and p-dimethylbenzene. Principally produced in petroleum refining. Colourless, flammable, with an aromatic odour.

Threshold Limit Value recommended by ACGIH, applicable in Ontario = 100 ppm (435 mg/m^3) - skin.*

The Ambient Air Criterion is 1 ppm. This is based on odour and takes precedence over health effects.

The xylenes have a low toxicity rating in man and animals. In man, they are irritant to nose and eyes at about 200 ppm and at this level, some narcotic effects are experienced.

Absorption is through skin, mucous membrane or lungs. Excretion is mainly by the kidneys, although some is excreted unchanged from the lungs. It is mainly metabolised to toluic acid and eliminated in congugated form with glycine as toluric acids. It does not accumulate in the body to a significant extent.

Liver and kidney damage have been reported after accidental ingestion of xylene-toluene paint thinner.

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* Skin - This refers to the potential contribution to the overall exposure by the cutaneous route, including mucous membranes and eyes by airborne or direct contact.

Reports of damage to the haemopoetic system are not substantiated: benzene has usually been a concomitant, and animals exposed to pure xylene have not suffered these effects.

No information is available on xylene in water supplies in relation to human toxicity.

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NAPHTHALENE

Toxicity

Oral child	LD_{LO}	100 mg/kg
Oral human	LD_{LO}	50 mg/kg
Oral rat	LD_{50}	1780 mg/kg

Aquatic Toxicity Rating TL_m 96 10.1 ppm
TLV - air 10 ppm 50 mg/m^3

Naphthalene is the most extensively used polynuclear hydrocarbon in industry. Toxicity data about this substance is very scanty. One of the major problems associated with naphthalene toxicity is its ability to trigger hemolytic crisis due to the presence of a genetically determined metabolic defect which is sex linked and finds full expression in the male(1). This disease would not exist in the absence of the challenging chemical yet naphthalene itself is nonhemolytic. A metabolite is indicated as the active compound. In older children and adults, the hemolytic crisis may be followed by renal tubular blockade and acute renal failure(7). In young infants the chief threat is Kernicterus, which causes high mortality(18).

Acute Toxicity

Rabbits given 1g/kg body weight daily develop changes in lens after three doses and definite opacity after 20 doses.

A case of human cataract has been reported, which may be a counterpart to those found experimentally in rabbits.

Vapor inhalation may cause headache, confusion, nausea and profuse perspiration. Systemic reactions have occurred after dressing children in clothing stored in mothballs(8).

Severe exposure or ingestion may cause vomiting, optic neuritis and hermaturia.

Chronic Toxicity

No chronic toxic effect have been reported as a result of industrial exposure to napthalene vapor and industrial poisonings are rare except for dermatitis due to hypersensitivity. No studies have been performed on animals with repeated inhalation.

In considering low level chronic exposures of humans to naphthalene, its world-wide household use during the last 100 years as "moth balls" should be noted.

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METHYLNAPHTHALENES

Unlike napthalene, the only reported effects of methylnapthalene in man are skin irritation and skin phtosensitization[1].

Oral human	LD_{50}	500 mg/kg
Oral rat	LD_{50}	4360 mg/kg

There appears to be a correlation between the degree of alkylation of the napthalene and its activity as a cocarcinogen and for this reason tri- and tetramethylnaphthalene are implicated as cocarcinogens with benzo(a)pyrene while methylnaphthalene is not[2].

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STYRENE (VINYLBENZENE)

Absorption

Styrene is readily absorbed from the lungs and slowly absorbed through the skin. No information is available on its absorption from the gastro-intestinal tract.

Toxicity

Short-Term Exposures

The acute toxicity of styrene is similar to other hydrocarbons. The most common toxic actions are irritation of the skin, eyes and respiratory tract and depression of the central nervous system. Stewart[4] reports mild eye and throat irritation developing in six male workers 20 minutes after the commencement of exposure to 99 ppm of styrene. At the end of a 7 hr. exposure period, which was interrupted for 30 minutes to simulate a workday, three of the six exposed workers had signs of neurological impairment, as evidenced by difficulty in performing a modified Rhomberg test.

Styrene vapors are irritating and narcotic at high concentrations and can produce nausea, headache, fatigue, dizziness and drowsiness. Stewart[4] found that concentrations of 216 ppm resulted in nasal irritation in one of five subjects. Exposure to 376 ppm for 1 hour was not tolerated, as the odour was objectionable and irritation occurred. Abnormal neurological findings were present within 1 hour of commencement of the exposure and nausea and headaches were experienced.

Chronic Exposure

Recent studies by Lindstrom[2] et al, have shown that exposure to styrene estimated at 75 ppm 8-hour time weighted average over a period ranging from 0.5 - 14 years, using mandelic acid excretion in the urine as an indicator of exposure was associated with disturbances in psychological functions (fisuomotor accuracy and psychomotor performances), and exposure to concentrations estimated at approximately 40 ppm 8 hour-time weighted average for a similar period was associated with abnormal EEG's in some subjects.[5]

Styrene oxide, a possible metabolite of styrene has been shown to have mutagenic effects for Salmonella typhimurium in vitro. However, there is no evidence of such effects in vivo to date.

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VINYL CHLORIDE

Absorption

Vinyl Chloride is absorbed following inhalation and injestion. Following absorption, vinyl chloride is believed to be metabolized to toxic metabolites which are detoxified in the liver before excretion. When large doses are encountered, however, this detoxification system is overburdened and the toxic metabolites accumulate.

Toxicity

Acute exposure to vinyl chloride can result in euphoria, a feeling of inebriety, somnolence, narcosis and in some instances, prolonged sleep. When acute episodes are repeated, headaches, irritability, diminution of memory, insomnia, paraesthesia and general anaesthesia can develop.[16]

Chronic exposure to vinyl chloride can result in effects on many of the body systems. Acroosteolysis* is frequently accompanied by vascular and skin changes.[19] Subcapsular and periportal hepatic fibrosis have been observed, and

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* Acroosteolysis - a condition in which dissolution of the terminal phalanges of one or more of the fingers is accompanied by clubbing, swelling and shortening of the nail beds and scleroderm-like skin changes.

are thought to be responsible for the portal hypertension and spenomegaly sometimes observed in those exposed.[18] These changes are also considered to predispose to hepatic tumor development, particularly hepatic angiosarcomas and perhaps heaptomas.[5] Both types have been observed in workers exposed to vinyl chloride.

Some epidemiological studies[14,15,21] suggest that the incidence of tumors of organs other than liver may be greater than expected in workers exposed to vinyl chloride.

There is also some evidence at the present time which suggests that exposure to vinyl chloride is responsible for the increased rate of congenital abnormalities observed in communities with PVC facilities.[9] Excess foetal wastage has been reported in wives of vinyl chloride workers and it is thought that this may be related to a germ cell effect of the chemical on the husbands.[10]

Studies concerning the chromosomal effects of vinyl chloride are inconclusive at the present time, some showing positive and others negative results.[6] Vinyl chloride has been found to be mutagenic in vivo in yeast systems,[12] in host (mouse) mediated assays and in somatic cells of Chinese hamsters.[6] Mutations have also been induced in vitro in activated bacterial and yeast systems.[8,12]

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1-2 DICHLOROETHYLENE

1-2 Dichloroethylene exists in two isomeric forms - a cis and a trans isomer.

Absorption

1-2 dichloroethylene is absorbed following inhalation, injestion and to some extent through the intact skin. Excretion is largely via the lungs in the unchanged form.(1)

Toxicity

Very little information is available on the toxicity of these isomers. Both are central nervous system depressants, which cause an initial irritation. The cis isomer is more irritant and less narcotic than the trans form.(1)

Animal studies indicate that fatty infiltration of the liver and pulmonary alveolar distension and hyperaemia are induced by single or repeated exposure to the trans form of the chemical.(2)

It is thought to sensitize the heart to adrenaline.(2)

No data on human toxicity, carcinogenicity, mutagenicity or teratogenicity of the chemical have been located.

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TRICHLOROETHYLENE

Absorption

Trichloroethylene is readily absorbed following ingetion and inhalation, but poorly absorbed through the intact skin. Trichloroethylene is lipid soluble, and as such, can be stored in body fat. Much of the absorbed trichloroethylene is eliminated unchanged in the expired air. Urinary excretion appears to be biphasic with a rapid first phase followed by a slow phase; the metabolites being present in the urine for more than 16 days after a 5-hour exposure to 100 ppm.(8)

Toxicity

Acute exposure to trichloroethylene results in depression of the central nervous sytem, which is frequently preceded by mild excitation. Symptoms of depression commonly encountered include: inebriation, uncoordination, dizziness, somnolence and in extreme cases, coma and death. If the chemical comes in direct contact with the skin, irritation and burns may result. Trichloroethylene sensitizes the heart to adrenaline and may induce cardiac arrhythmias. Some incidences of sudden death associated with acute exposure have been attributed to ventricular arrhythmias induced in this manner.

Subacute exposure of humans to trichloroethylene (two 4-hour periods separated by a 90-minute interval, to 110 ppm) have resulted in alterations of psychophysical function.[9]

Chronic exposure continued over a period of years appears to affect the nervous system; the symptoms most commonly encountered being giddiness, headaches, insomnia, tiredness, disturbances of the autonomy nervous system, inability to tolerate alcohol and physical changes.[4]

Studies conducted by Takametso, Nomura Capellini and Grisler, Graovad-deposavic et al[8] indicate liver damage following exposure to trichloroethylene for more than 5 months. However, it is presently thought that the chemical is not hepato or Reno toxic.[8]

Studies on the carcinogenic properties of trichloroethylene are inconclusive. The study undertaken by N.C.I. indicates that it is carcinogenic in mice, whereas, other studies indicate it is not.[8] There is no indication at the present time that trichloroethylene is carcinogenic in man.[2]

Mutagenic testing indicates that trichloroethylene is mutagenic, after activation, in bacterial[5] and yeast test systems.[3] No studies have been located on teratogenic effects of trichloroethylene.

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TETRACHLOROETHYLENE

Absorption

Tetrachloroethylene is absorbed percutaneously, following inhalation and ingestion. It is lipophilic, and as such, is stored in body fat. Because of this, the whole body half life is such that a period of 2 weeks may be required to eliminate the tetrachloroethylene retained after an 8-hour exposure to 100 ppm.[1]

Toxicity

Tetrachloroethylene is a conjunctival, upper respiratory tract and skin irritant. Acute exposure causes central nervous depression as manifested by dizziness, light headedness, vertigo, inebriation, nausea, impaired coordination, liver damage, coma and death.[2,6]

Repeated or prolonged skin contact with the chemical may cause erythema blistering and skin burns. Chronic inhalation of concentrations greater than 100 ppm are reported to cause only term effects on the central, peripheral and autonomic nervous systems. Confusion, impaired memory, tremors, numbness of

the extremities and peripheral neuropathy have been reported. Liver damage has also been reported in workers chronically exposed.[6,7,8]

Some studies indicate that tetrachloroethylene is a carcinogen in mice.[9] However, other carcinogenic studies do not support this finding.[5,6] There is no evidence at the present time which shows tetrachloroethylene to be carcinogenic in man. Mutagenicity testing in bacterial test systems, with and without activation was negative for tetrachloroethylene.[10,11]

There is some evidence to indicate that tetrachloroethylene is fetotoxic in mice but not rats.[12] However, there is only one animal study and no human studies available on this aspect of its toxicity.

TETRACHLOROETHYLENE - BILIOGRAPHY

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MONOCHLOROBENZENE

Toxicity

Oral LD_{50} rat - 2910 mg/kg
Ipr LD_{LO} rat - 7400 mg/kg
Oral LD_{50} rabbit - 2830 mg/kg
Ipr LD_{LO} guinea pig - 4100 mg/kg

Aquatic Toxicity Rating TLM 96: 100-1 ppm
TLV - air - 75 ppm 350 mg/m^3

Monochlorobenzene is a CNS depressant that may cause symptom typical of the analgesic effect. It is not known to cause the blood changes typical of benzene exposure. Liver and kidney injury have been noted and the liver injury may progress to necrosis and parenchymous degeneration.

Although there are no indications of toxic absorption through the skin, direct application does cause reddening and continuous contact (for more than 1 week) and may cause erythema and superficial necrosis.

Animal Studies

At 0.0144 g/kg body weight and0.288 gm/kg, there were significant increases in liver weight and evidence of liver histopathology.

Dow Chemical Co. exposed rats, rabbits and guinea pigs 7 hrs/day, 5 days/week, for a total of 32 exposures over 44 days at 1000 ppm in air. They found histopathological changes in lungs, liver and kidneys plus a slight depression in growth. Mortality increased in the guinea pigs, but not in the rats or rabbits; at 475 ppm the guinea pigs survived and at 200 ppm everything appeared normal.

Rabbits receiving a dose of 0.5 g/kg excreted 27% unchanged in their expired air, while all but 1% of the rest was excreted in the urine.

O-DICHLOROBENZENE

An agricultural chemical herbicide of indefinite carcinogenic determination.

Toxicity

Oral human LD_{50} - 500 mg/kg
Oral rat LD_{50} - 500 mg/kg
Ihl rat LD_{LO} - 521 ppm/7H
Oral rabbit LD_{50} - 500 mg/kg
Oral guinea pig LD_{LO} - 2000 mg/kg

TLV - air 50 ppm

The ortho-isomer is said to be more toxic than the paraisomer of dichlorobenzene. The primary human physiological response to this isomer is injury to the liver and secondarily, to the kidney. The compound acts as a liver and kidney poison as well as being a local irritant and a strong CNS depressant.

Animal Studies

Acute Vapor Exposure

Rats survived 2 hours at a concentration of 977 ppm in air and succembed after 7 hours. They survived 7 hours at 539 ppm exposure, however, they became drowsy and unsteady. There was an increase in liver and kidney weight accompanied by marked central locular damage to the liver and the tubular epithelium of the kidneys.

Chronic Vapor Exposure

Animals exposed 7 hours/day, 5 days/week to 93 ppm survived 6 to 7 months without any effects on growth, organ weight, hematology or histopathology. The main effect here was eye irritation and moderate pain, which cleared in a few days.

Human Experience

Odour is detectable at concentrations above 50 ppm but eye and nose irritation is not noticeable at this level.

P-DICHLOROBENZENE

An insecticide and disinfectant as well as a chemical intermediate. This compound is the least toxic active ingredient found in mothballs.

Toxicity

Oral human LD_{LO} - 500 mg/kg
Oral human TD_{LO} - 300 mg/kg
Oral rat LD_{50} - 500 mg/kg
Oral guinea pig LD_{LO} - 2800 mg/kg

TLV - air - 75 ppm. 450 mg/m^3

As in o-dichlorobenzene, the primary physiological effect here is liver damage and then, kidney damage. CNS depression does not occur until concentrations are highly disagreeable to the eyes and nose.

Absorption

This compound is absorbed through the G.I. tract and through the lungs, but there is no evidence of absorption through the skin.

Animal Studies

Vapor Exposure

Rats, rabbits and guinea pigs exposed 5 days/week, 7 hours/day for extended periods at 798 ppm exhibited definite toxic reactions - tumors, weakness, weight loss and eye irritation. At 341 ppm, animals survived 6 months with slight growth depression in guinea pigs, accompanied by pathological changes in the liver and

increased liver weights in the case of the rats. At 96 ppm, no adverse effects were demonstrated.

Solid vapor particles or fumes are all very painful to the eyes and nose. At 50 to 80 ppm, discomfort is quite severe.

Human odour threshold is 15 - 30 ppm.

The following summary data was obtained from "Dangerous Properties of Industrial Materials", by N. I. Sax, Fifth Edition, 1979, published by Van Nostrand Rheinhold. The codes are as follows:

Low - causes readily reversible tissue changes which disappear after exposure stops. Causes some discomfort.

Mod. - may cause reversible or irreversible changes to exposed tissue, not permanent injury or death. Can cause considerable discomfort.

High - capable of causing death or permanent injury due to the exposures of normal use; incapacitating and poisonous. Requires special handling.

METHYLENE CHLORIDE

Mod. via oral, intraperitoneal, subcutaneous and inhalation routes. An experimental carcinogen. Dangerous to eyes. Few acute toxicity effects other than the inducement of narcosis.

Acute toxicity data:

Oral LD_{50} (rat)	2136 mg/kg
intraperitoneal LD_{50} (mouse)	1500 mg/kg
subcutaneous LD_{50} (mouse)	6440 mg/kg
inhal LC_{LO} (guinea pig)	5000 ppm for 2 hours
inhal TC_{LO} (humans)	500 ppm for 8 hours (blood problems); prolonged exposure at this level causes CNS problems

CHLOROFORM

Mod. via oral and inhalation routes. An experimental carcinogen and promoter of neoplasms.

Acute toxicity data:

oral LD_{50} (rat)	800 mg/kg
inhal LC_{LO} (rat)	8,000 ppm for 4 hours
inhal LC_{LO} (mouse)	28 ppm

BROMODICHLOROMETHANE

Unknown. Probably narcotic in high concentration.

BROMOFORM

High via subcutaneous route. Is narcotic and causes lachrymation. Can cause liver damage and is a metabolic poison.

Acute toxicity data:

subcutaneous LD_{50} (mouse)	1,820 mg/kg

CARBON TETRACHLORIDE

Mod. via oral, intradermal and inhalation routes. High via human oral and inhalation routes. Less narcotic than chloroform.

Acute toxicity data:

oral LD_{50} (rat)	1770 mg/kg
intraperitoneal LD_{50} (rat)	1500 mg/kg
inhal LC_{50} (rat)	9526 ppm for 8 hours
oral LD_{LO} (humans)	60 mg/kg
inhal TC_{LO} (humans)	20 ppm (CNS problems)

1,1,1-TRICHLOROETHANE

Mod. via intraperitoneal and oral routes. Narcotic in high concentration.

Acute toxicity data:

intraperitoneal LD_{50} (mice)	4700 mg/kg
oral LD_{50} (dog)	750 mg/kg
oral LD_{50} (rabbit)	5660 mg/kg
inhal LC_{LO} (man)	27,000 mg/m^3 for 10 min. 920 ppm for 70 min. causes CNS effects in humans.

DICHLOROPROPANE

Mod. via oral, inhalation and dermal routes. Can cause dermatitis and is regarded as one of the more toxic chlorinated hydrocarbons.

Acute toxicity data:

oral LD_{50} (rat)	1,900 mg/kg
inhal LC_{LO} (rat)	2,000 ppm for 4 hours
dermal LD_{50} (rabbit)	8,750 mg/kg

BENZENE

Poisonous, often characterized by narcosis resulting from action on CNS. Recognized leukemogen. Has a cumulative action: sporadic exposure to relatively high concentrations is not serious from the point of view of causing damage to the blood-forming system; prolonged exposure to concentrations of 100 ppm or less may cause damage.

TOLUENE

Mod. via oral, inhalation and intraperitoneal route. Low via dermal route. Acute toluene poisoning is characterized by narcosis. Recovery following removal from exposure is normal.

Acute toxicity data:

inhal TC_{LO} (human)	200 ppm (CNS effects)
inhal TC_{LO} (man)	100 ppm (psychotropic effects)
oral LD_{50} (rat)	5,000 mg/kg

inhal LC_{LO} (rat)	4,000 ppm for 4 hours
intraperitoneal LD_{50} (rat)	1,640 mg/kg
inhal LC_{50} (mice)	5,300 ppm
dermal LD_{50} (rabbit)	14,000 mg/kg

TRIMETHYLBENZENE

1,2,3: Mod. via oral route.

Acute toxicity data:

LD_{LO} (rat)	5,000 mg/kg

1,2,4: Mod. via oral and intraperitoneal routes. Mod. - low via dermal route. Can cause CNS depression, anemia and bronchitis.

Acute toxicity data:

oral LD_{LO} (rat)	5,000 mg/kg
intraperitoneal LD_{LO} (rat)	2,000 mg/kg

1,3,5: Mod. via intraperitoneal and inhalation routes. Causes CNS disturbances, animal experiments show narcotic effects and blood disturbances.

Acute toxicity data:

inhal LC_{LO} (rat)	2,400 ppm for 24 hours
intraperitoneal LD_{LO} (rat)	1,500 mg/kg
inhal TC_{LO} (human)	10 ppm (CNS effects)

CUMENE

Mod. via oral and inhalation routes. Potent narcotic and CNS depressant. Possibly has greater acute toxicity than toluene or benzene.

Acute toxicity data:

oral LD_{50} (rat)	1,400 mg/kg
inhal LC_{50} (rat)	8,000 ppm for 4 hours

DIETHYLBENZENE

Low to mod. via oral route.

Oral LD_{LO} (rat)	5,000 mg/kg

ACETONE

Mod. via oral, intraperitoneal and inhalation routes. Very low via dermal route. Narcotic in high concentrations.

Acute toxicity data:

oral LD_{50} (rat)	9,750 mg/kg
dermal LD_{50} (rabbit)	20,000 mg/kg
intraperitoneal LD_{50} (mouse)	1,297 mg/kg
inhal TC_{LO} (human)	500 ppm (eye symptoms)

The text suggests that the toxicity of chlorinated hydrocarbons increases in the following order:

Methylene chloride
Trichloroethylene
Carbon tetrachloride
Dichloropropane
Dichloroethane

Appendix 3

The Effects of Aqueous Chlorination

Appendix 3

The possible formation of chlorinated compounds during disinfection of drinking water has been the subject of much debate. Chemically the aqueous chlorination of aromatics appears unlikely but has, in fact, been demonstrated on several occasions. There is a considerable amount of evidence to indicate that the trihalomethanes (chloroform, bromodichloromethane, chlorodibromomethane and bromoform) are produced on chlorination and the precursors are believed to be natural products, such as humic acids. This report contains additional data to support this theory: for example, the routine monitoring data (Tables 71, 72, 73) demonstrate that the concentration of trihalomethanes is invariably higher than in the raw water. The data also suggests that carbon tetrachloride is not produced by this mechanism since it is usually found on both raw and treated water. Similarly, methylene chloride appears to be the result of industrial activity, because it is a very common solvent, and may reach the receiving water by aerial transport.

Several studies have been performed in OTC to examine the aqueous chlorination of aromatics. Initially the work considered the chlorination of biphenyl since the likely products (PCB's) are known to be a significant health hazard. The results ("Aqueous Chlorination of Biphenyl - significance for chlorination in Sewage Treatment Plants", by R. Bonner, O. Meresz, T. Sakuma and B. Shushan, March 1978) indicated that chlorination does occur, with surprising speed, but that the conditions prevailing in Sewage Treatment Plants (STP's) is likely to reduce the reaction rate, and hence the impact, enormously because of competing reactions for the available chlorine. A variety of other aromatics, including toluene, xylene and styrene, have been examined. All were found to chlorinate but in no case were haloforms detected as products.

In summary, then, aqueous chlorination is well established as giving rise to trihalomethanes but the levels are generally very low.

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